PETROLEUM REFINER

SPECIALIZED FOR THE OIL REFINING INDUSTRY, INCLUDING PETRO-CHEMICAL ENGINEERING, PETROLEUM SYNTHETICS AND NATURAL GASOLINE

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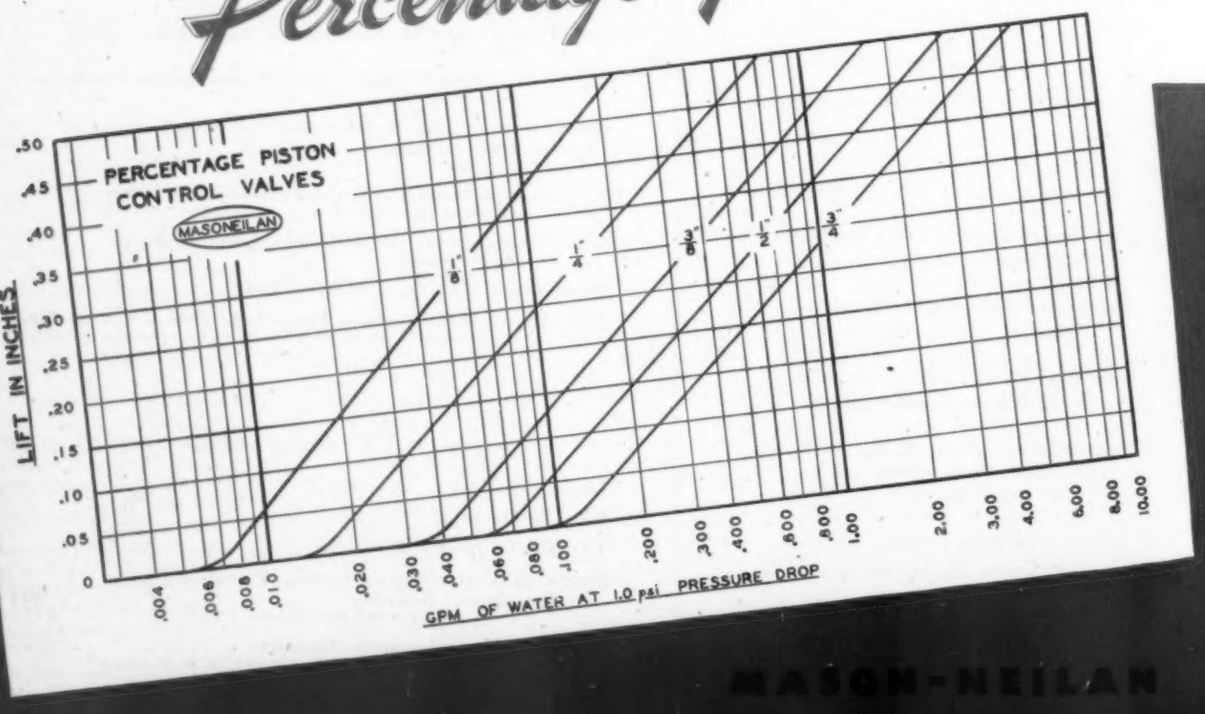

MASON-NEILAN

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THE LOOK BOX

IN HIS acceptance of the 1946 gold medal of the American Institute of Chemists, Robert P. Russell, president of Standard Oil Development Company, pointed to the fallacy of the agitation to prevent private research from gaining patent rights when it functions along with government.

Public Interest

"The root of this idea," he explained, "is the sound premise that no one should profit from projects financed with public money. No one questions that this premise is entirely reasonable. In actual operation, however, I am afraid that provisions intendent to insure it would react against the public interest and would fatally handicap work for the armed forces."

He mentioned pending legislation which would require any industrial agency, when on important government research, to surrender all patent rights.

"Under these conditions," he added, "I believe that many research and development groups would be practically prohibited from undertaking work for the government in fields of their own commercial interest, which incidentally are the fields of their outstanding competence, for it would be difficult, if not impossible to separate patent rights paid for by the government from those stemming from the normal commercial developments of the company."

After noting that existing law already provides that no patent can block the government from taking what it needs for its own use, he concluded:

"During the war government, science and industry worked as a well-coordinated team and I am certain that no member of the team has any intention today of weakening that cooperation. Therefore, I am convinced that a formula can and will be found which will safeguard the public interest and at the same time give our industrial research and development agencies the freedom and incentive to cultivate vigorously the new scientific fields in which American technical genius was largely instrumental in breaking the soil."

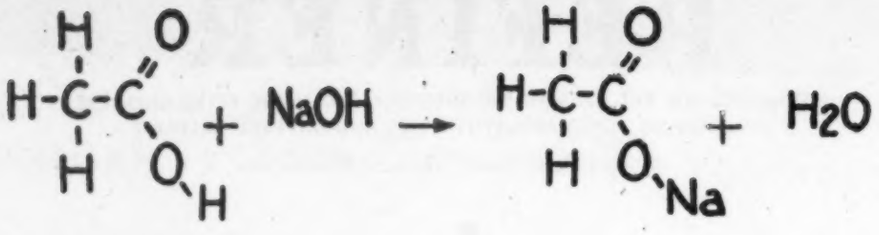
MORE distressing than the strikes that beset the American economy is the plight of individuals, whose wages stop when work stops. There is a temptation to class the worker as a victim but his recent attitude classes him as a willing pawn of one or a few men. One man speaks and a horde agrees. They cease working when he commands; they resume work when he gives the word.

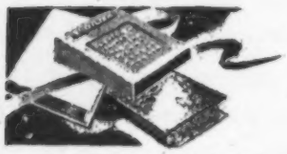
Willing Pawns

Doubtless there are workers who resent the system. But they do not openly oppose the scheme whereby one man or a clique dictates the policy. Fear may be partly responsible for this submission. In larger measure it must be that men consider it good to surrender their rights in return for wage increases.

Wages, whatever their height, are not worth the freedom that is handed over when one man or a few men come into the authority now accepted by the labor leader. Men become arrogant when

AS CERTAIN AS





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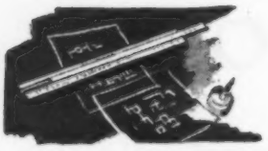

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given authority and their arrogance is despicable when it applies to the lives of other men. Labor leaders are not immune from this arrogance, which is the reason for public wrath.

When men gain such power in politics they are branded as dictators, such as those who recently paraded over Europe until war destroyed them. The war was a frightful price to pay for removing two men from high places.

When men gain such power in lesser affairs, labor business or what else, they are dictators and nothing short of drastic action will remove them, so long as men are willing to submit.

His Own Protector

NOTHING could match the attitude of the bureaucrat in his inconsistency. Invariably when he has an inning at the microphone or gains newspaper space, he justifies his efforts as "in the public interest." He, by his own designation, has been set up to take care of men and women, who thereby gain the rank of inability in their own right.

But no one is better equipped to take care of himself than the man or woman, thus belittled.

OPA operates, so its backers claim, to protect the customer. Yet the customer, give him freedom to buy where he chooses, can take care of himself without assistance. Give him or her two places from which to buy and give each of the places freedom to fix its own prices and the customer will take care of himself.

Ready to Go Places

NEVER have the drafting boards been so laden with plans for refining units. Even the hectic war period offered nothing to compare with the desire to build new units, revamp old ones and otherwise bring the physical equipment of refining up to current and indicated demands of automotive engines.

The plans, some finished and bids sought, others finished but put away in hope of more favorable conditions, some still in that stage of mental speculation, will rehabilitate an industry. They include new catalytic-cracking units, large and small; new lubricating-oil plants; new cycling and natural-gasoline plants; new petro-chemical processing plants.

The desire, even the determination, to build surpasses anything the industry previously has known.

How to do it in the face of material shortages, strikes and the tamer work stoppages, is a baffling problem. One set of men has opportunity to build; another hesitates and there is scant building. One set of men would provide equipment to power automobiles, yet to be built; until recently the automobile mechanic did not care to work.

American industry can point to nothing like it. Ordinarily the determination to build a new plant, even to revamp an old one, could be accepted as a boon to a community. Now it is simply a plant, either on a drafting board or in imagination.

And those who hesitate seem assured that once they decide to return to their tasks the drafting boards will still be burdened. There is such a thing as waiting too long.

Assistance From Sand

IT IS being called "white carbon black" because it serves in rubber as the black from natural gas serves. But the white soot comes from sand by a process worked out in the laboratory of B. G. Goodrich Company.

What is meant is that some of the drain on carbon black now can be shifted to the white ingredient in the compounding of finished rubber goods. Furthermore the white product can be colored and thus give rubber a wider appeal.

And carbon black needs some assistance in the rubber field, where a billion pounds of it will be used this year. When first used in 1911 consumption was a million pounds.

Precious Resource

IN THE concern over possible exhaustion of petroleum resources little attention is given to a more potent resource—research. If left unhampered research will provide adequate substitutes long before petroleum resources are exhausted. No one knows how much oil remains for finding. Fortunately a few know that research can supplant what no one knows about oil. By its record research stands as our most precious resource. Its value was well outlined by Dr. Robert E. Wilson, Standard Oil Company (Indiana) in his appearance before the special Senate committee on petroleum resources:

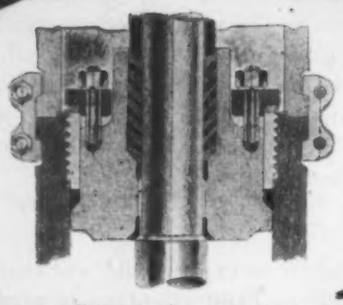
"The one point I want to emphasize is that our most important reserve does not consist of the number of barrels of oil that we can point to in the ground, but rather of research and technology supported by a healthy and vigorous industry. Technology is the indespensable finder, developer and multiplier of our natural resources and given a fair chance will accomplish even more in the future than it has in the past. The most essential element of national oil policy is to leave the industry free to develop on a tried and proven basis and to shun the adoption of measures which would attempt to regiment research, destroy the incentives to innovation, or prevent the free play of competitive enterprise."

New!

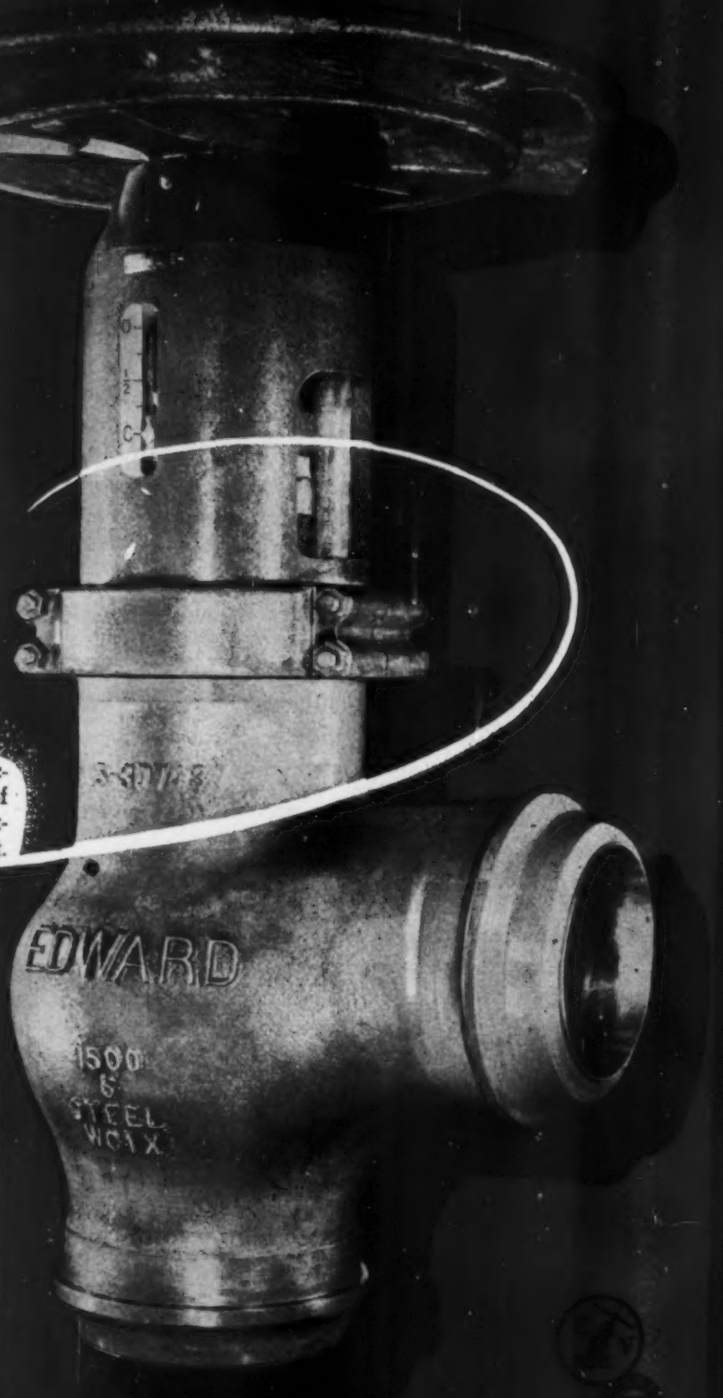
TWO Edward Designs FOR TOP PRESSURE-TEMPERATURE OPERATING CONDITIONS

PRESSURE-SEALED BONNET VALVES

NON-RETURN VALVE, at right, shows Edward pressure-seal design. Valve incorporates flow directional guiding, internal contouring for extremely low pressure drop, closure indicator and Edward Impactor handwheel.



Principal parts of pressure-seal connection. This construction cuts weight of standard high pressure, high temperature valve by as much as 50 per cent.



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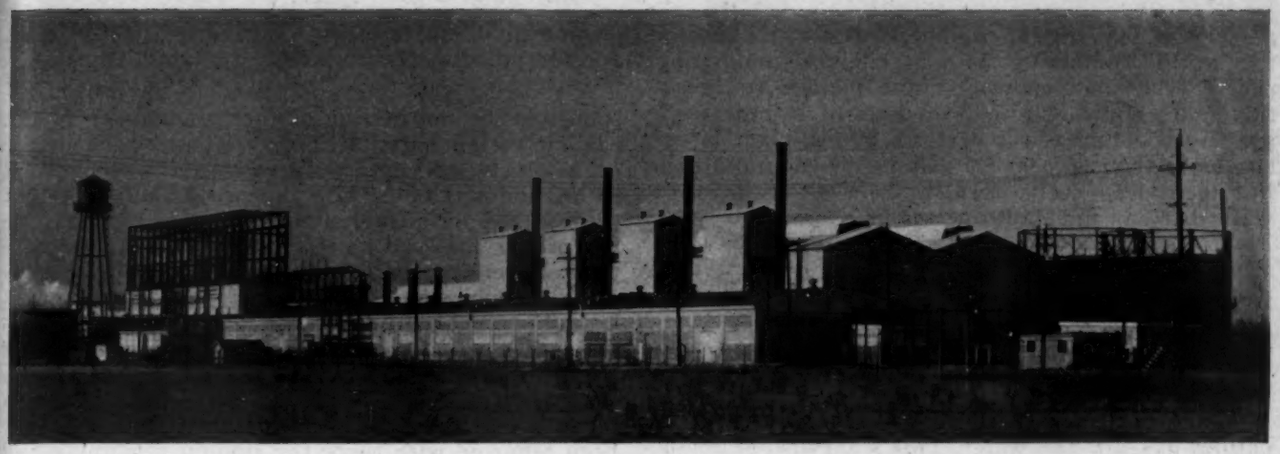


FIGURE 1
Ammonia Plant—Lion Oil Company, Chemical Division, El Dorado, Arkansas

AMMONIA

Its Production

From Natural Gas

GUY S. MITCHELL, Chief Chemist
Chemical Division—Lion Oil Company

THE manufacture of synthetic nitrogen compounds has assumed a major role in the current of industrial events in the last few years, quite in contrast to the conditions in this country during World War I. At that time, the chief source of nitrogen was from Chilean nitrate. However, the close of that war and the years that followed saw the United States instituting an extensive program in synthetic nitrogen research and development work. Therefore, at the outbreak of World War II, the country was all set for a program of expansion and, in the months prior to Pearl Harbor, plans were made for establishing a synthetic-nitrogen industry which would care for ammunition requirements. The rapidity with which this industry has grown is astonishing for in a comparatively short time the production was trebled and reached approximately 1,500,000 tons of nitrogen in 1944.

As a part of this vast program we find that on October 10, 1941, the War Department authorized the Lion chemical plant, formerly known as Ozark Ordnance Works, an ammonium nitrate plant, to be operated by Lion Chemical Corporation, El Dorado, Arkansas, a wholly-owned subsidiary of Lion Oil Company. Actual construction of the plant required less than 13 months, and operations were begun May 13, 1943. The Lion plant, completed and operating these many months, is a plant of beauty in design and workmanship, well arranged, of sturdy construction, and one whose cost ran into the millions of dollars. The plant was one of eight Ordnance ammonia plants, five of which, including the Lion plant, have utilized natural gas reforming as a source of hydrogen.

The plant, Figure 1, came under private operation May 13, 1946, under a long-term lease to Lion Oil Company, whose newly created chemical division will supervise operations. This contract, which carries an option of purchase, calls for the construction of a new unit for the production of finished ammonium nitrate fertilizers. Meanwhile the company has leased temporary graining facilities at Minden, Louisiana, and Texarkana, Texas. Full operation of the plant will include anhydrous ammonia, fertilizers and other synthetic chemicals.

More than 6000 drawings and 40,000 prints were made in designing the Lion plant. There were 82,000 cubic yards of concrete, 42,000 tons of steel, 480,000 square feet of asbestos sheeting, and 633,000 feet of electric wire used in constructing the plant. Over 5000 men were employed at peak construction, and a total of more than 9,000,000 man hours required. Twenty-, fifty-, and eighty-ton towers were erected, ranging from 60 to 72 feet high. The plant includes a

Atmospheric nitrogen is available in inexhaustible quantities. To convert this vast store of nitrogen into a raw material for the manufacture of indispensable fertilizers and peace time as well as war time explosives has been one of the major tasks of the chemist. He has discharged it brilliantly. Of the total compounds made or extracted for their ntirogen values, 73 percent are "chemical nitrogen" or "air nitrogen" compounds.

Reigel "Industrial Chemistry," 1942.

gas engine building, one of the largest of its kind in the world, containing 54 gas engines comprising nearly 60,000 horsepower. These include refrigeration units equivalent to 3000 tons of refrageration per day. Cooling tower systems in the plant circulate more than 150,000,000 gallons of water per day. Fourteen deep wells furnish 3,500,000 gallons of water per day for plant operations and sanitary use. Plant operations consume more gas than a city the size of Boston. A panoramic view of the completed plant reveals more than 25 principal buildings.

Economic Considerations

A synthetic ammonium nitrate plant such as the Lion plant requires only three raw products namely—natural gas, air, and water. This plant also is unique in the fact that the design of the plant included not only the use of natural gas as a source of hydrogen but also as the prime source of fuel. We find the natural gas therefore being used as fuel for steam production, as fuel for gas engine driven refrigeration and process compressors, as fuel for gas engines in electric power generation, and as fuel for gas engines driving process water pumps. This is an important economic consideration since the plant is located in an area of abundant supply of natural gas of high quality. Furthermore, low price natural gas is of major importance in the production of low cost ammonia, since one fourth of the total manufacturing cost of Lion ammonia is due to the cost of natural gas consumed. An ample supply of good water, a dependable source of labor, adequate railway facilities, and strategic location in respect to Ordnance ammunition facilities to be serviced were other contributing factors to location of the Lion plant at El Dorado. An important postwar economic consideration is the fact that this plant is strategically located in respect to the fertilizer-consuming areas.

Makes Enviable Record

Wise designing, ruggedness of construction, low-priced raw material, favorable economic considerations, and efficiency in operation certainly spell production records, and such is the history of the Lion plant. This plant led the Ordnance plants and perhaps the industry throughout the world in low production cost for the manufacture of ammonia. Furthermore, this plant was the largest producer of ammonia among the various Ordnance facilities. Month after month the plant established new records in low production cost and quantity production. In recognition of this record, the plant was awarded the Army-Navy "E" May 5, 1944, and since then has been presented two stars to add to the award.

History of Synthetic Ammonia Process

Early in history, we find man restoring the fertility of the soil in respect to its nitrogen content by plowing manure into the soil and also by the use of legumes such as clover and beans. This he did without fully understanding the principle involved. However, we now know that legumes, whose roots harbor nitrogen fixation bacteria, fix as much as 60 pounds of atmospheric nitrogen per acre per year, and this amount is a sizeable fertilizer treatment for the soil. This is a part of the elaborate nitrogen cycle which goes on in nature. The soil receives nitrogen from the above and various other sources, bacteria in the ground gives up nitrogen, plants take up nitrogen, and the process continues to be repeated.

A growing population is found to have been responsible for the decline of the productivity of the earth in certain parts of Europe so that by the middle of the nineteenth century a need for nitrogen addition to the soil was being felt. It was, at this time, that Chilean sodium nitrate stepped into the picture. The use of this material as fertilizer began in the early part of the nineteenth century by the South American Indians. Some years later, the nitrate was brought to the world's attention when several Europeans discovered these Indians using the material as fertilizer. These beds of sodium nitrate are said to be 400 miles long, 5 to 40 miles wide, and 5 to 25 feet underground. More than 100,000,000 tons have been removed with twice the amount remaining and large regions unexplored. It may be said that Chilean nitrate has had its "hey-day," but it has been a boon to civilization, being introduced on the market when little other commercial nitrogen fertilizer material was available. The synthetic-ammonia industry, however, has been responsible for synthetic or chemical nitrogen products, rapidly replacing sodium nitrate in many parts of the world.

Fixation of nitrogen began with Cavendish in 1780 when he caused nitrogen and oxygen to combine by means of an electric spark. The first attempt at using this process commercially was by Bradley and Lovejoy at Niagara Falls in 1902. The first successful process was established in Norway a few years later, and its success was due to the use of a larger arc flame area and faster removal of gases from the reaction chamber than was used in the American process.

As early as 1839, Kuhlman found that the oxidation of ammonia could be made to take place by the aid of a contact substance such as platinum at a temperature of 300° C. In 1900, Ostwald began a study of this process and in 1908, the first commercial unit was placed in operation in Germany. This was followed by another plant in Belgium in 1912. Four years later, the first American plant, although a small one, was built at Niagara Falls. Following this, a commercial size unit was built at Warners, New Jersey. In this same year, 1916, the United States government entered the field and plants were built at Sheffield, Alabama. Progress has been rapid in this field so that today synthetic ammonia oxidation is the prime source of nitric acid.

Manufacture of synthetic ammonia was first attempted about 1903. It was developed and put into operation in Germany in 1913, the process being known as the Haber-Bosch process. Dr. Haber is credited with the synthesis or catalytic conversion of the hydrogen-nitrogen mixture to ammonia, while Dr. C. Bosch developed the problem of supplying a cheap source of raw gases in large quantities as required by the process. The process has furnished the chief source of nitrogen for Germany through two World Wars. The source of hydrogen was water gas from coke and producer gas from low grade coal. Iron oxide catalyst, containing small amounts of chromium and cerium was used for conversions of carbon monoxide in these gases to hydrogen. The producer gas also furnished nitrogen for the process. Purification of the gas was done at high pressures by means of water scrubbing, caustic scrubbing, and copper ammonium formate solution scrubbing. Synthesis was accomplished at 2950 pounds pressure and

500° C. (932° F.) in the presence of a promoted iron catalyst.

Various modifications of the above processes for the fixation of nitrogen have been developed, and, in addition to these, there are also the cyanamide, cyanide, ferrocyanide, and nitride processes. Aside from the synthetic ammonia process, the cyanamide is the only one which has been of much commercial

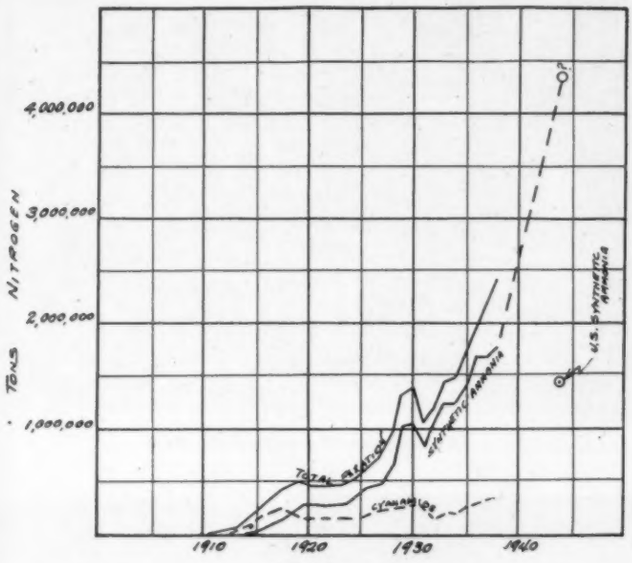


FIGURE 2
Growth of atmospheric nitrogen fixation for the world

importance as is shown by the graph given in Figure 2. This chart also illustrates the rapid growth in the manufacture of synthetic nitrogen compounds.

Synthetic Ammonia and Ammonium Nitrate

It is readily seen that nitrogen fixation is the most logical of all methods for the production of nitrogen compounds when we consider the fact that there is an inexhaustible supply of the basic material, nitrogen, in the atmosphere. We find that 22,000,000 tons of nitrogen rest on each square mile of the earth's surface. The only other raw materials required for a process such as at the Lion chemical plant for manufacturing synthetic ammonium nitrate are natural gas and steam. Therefore, since there are large natural gas reserves in the United States, we may be safe in saying that there is an abundant supply of raw materials, for processes such as the above, sufficient to supply the country's nitrogen needs for many years.

This process consists of six principal steps as follows: (1) manufacture of the raw 3:1 hydrogen-nitrogen gas mixture, (2) purification of the gas mixture, (3) synthesis of the purified hydrogen-nitrogen gas to ammonia, (4) recovery of ammonia vapors from purge gases, (5) ammonia oxidation for the manufacture of nitric acid, and (6) neutralization of the nitric acid with ammonia for the manufacture of ammonium nitrate solution.

Raw Gas Manufacture

The manufacture of the raw gas or suction gas as it is termed is accomplished by reacting methane with steam, introducing air for the nitrogen, and producing additional hydrogen by reacting CO with steam.

The natural gas, when of high purity containing only a trace of hydrogen sulphide and/or organic sulphur compounds, is brought direct to the reform plant where the raw gas is made. Here the natural gas first passes through an interchanger picking up heat from hot process gas. From this unit it goes to the organic sulphur removal vessels at 350-400° C. (662-752° F.) for purification of the natural gas by contact with zinc oxide to remove all traces of sulphur compounds. Steam passes through an interchanger similar to that mentioned above, and the natural gas and steam go to a mixer where the two are mixed prior to being distributed to the reform tubes. The gas and steam mixture is fed to a reform furnace containing the catalyst tubes. Passing through these tubes over a nickel catalyst at approximately 700° C. (1292° F.) and with 100-150 percent excess steam above that required for the reaction, the methane and other hydrocarbons are reformed into hydrogen.

The primary reformed gas then passes to the secondary reformer. Here nitrogen air is introduced, the oxygen consumed, and additional methane reforming obtained in the presence of a nickel catalyst. The secondary reform gas at approximately 1000° C. (1832° F.) passes through a waste-heat boiler for cooling the gases. Low-pressure steam is introduced in the desired amount (approximately 3 pounds per hour per cfm of gas), and the mixture passed to the CO converter. Here in the presence of a promoted iron-oxide catalyst the carbon monoxide reacts with the steam to form hydrogen.

The hot gases leaving the CO converter at approximately 525° C. (977° F.) pass through the natural gas and steam interchangers, and then to a gas-cooling tower where the gas is cooled to atmospheric temperature by direct contact with water. The gas exit the cooling tower is the raw impure 3:1 hydrogen-nitrogen mixture, and moves into the header on the suction gas line, which goes to the suction gas holder and the compression plant.

The chemistry of the reforming process and preparation of the raw gas is explained by a few simple equations. Excess steam is required in the reforming to guard against the deposition of carbon on the catalyst with resultant spalling and disintegration of the catalyst material.

$$CH_4 \rightleftharpoons C + 2H_2 \quad (1)$$

The primary reform reaction is a combination of several reactions as shown in equations 2, 3, and 4.

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad (2)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (3)$$

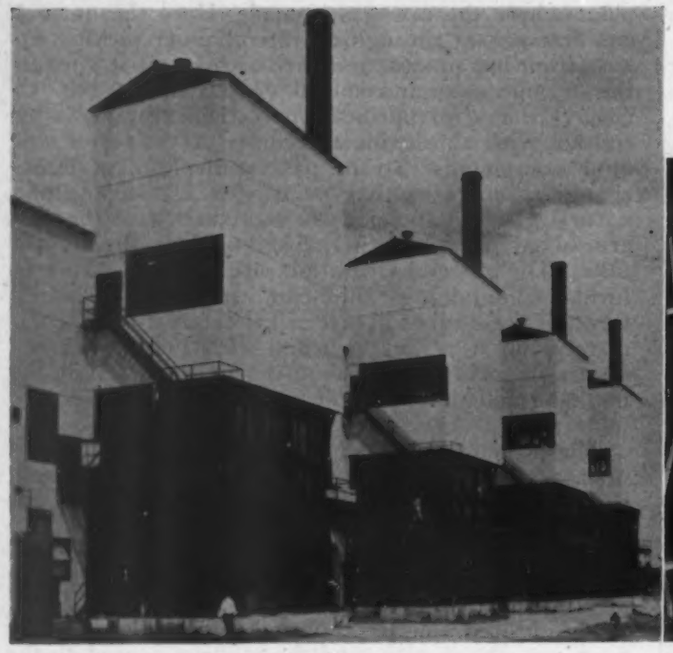
$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \quad (4)$$

Equation 4 is the overall equation for reactions 2 and 3. Careful control of reform operating conditions will result in attainment of reforming surprisingly close to equilibrium. In general, normal operation will result in reforming of the methane in quantities of approximately 50-50 according to equations 2 and 4. For equilibrium calculations perhaps the most simplified procedure is to assume all reformed hydrocarbons to follow equation 2 and then solve for the amount of CO reached according to equation 3. Reaction 2 is highly endothermic while reaction 3 is exothermic.

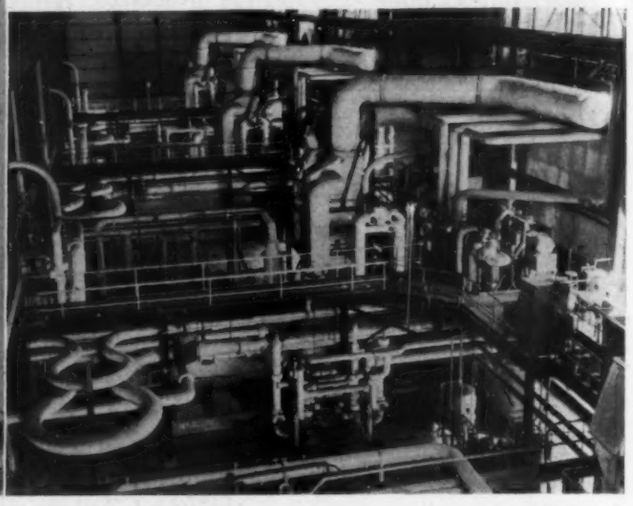
Equilibrium conditions for the reactions 2 and 3 are shown in the charts given in Figures 3 and 4. Figure 3 shows the variation in mols of methane reacted per 100 mols of (reaction) natural gas, and mols of carbon dioxide formed per 100 mols of natural gas for various steam/gas ratios at the various temperatures. Note the sharp break in the methane curves in the region of 740-760° C. The curves show that for a steam/gas ratio of 4 mols steam per

Reform Plant

(Location of these views may be identified on opposite flow chart.)

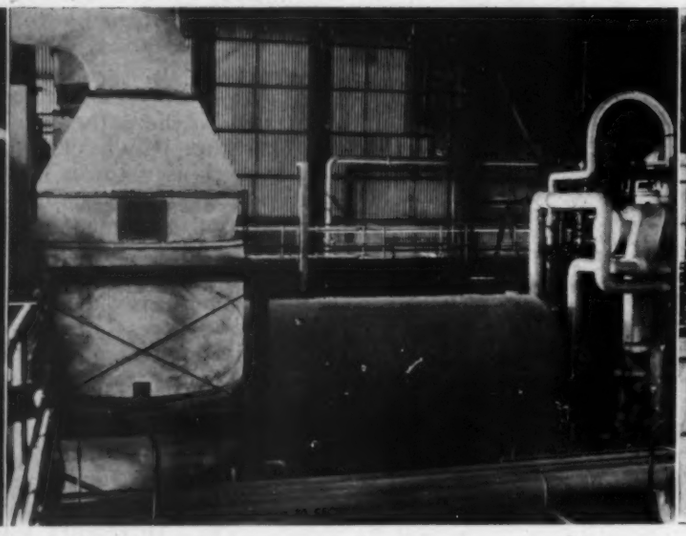


Primary reform furnaces

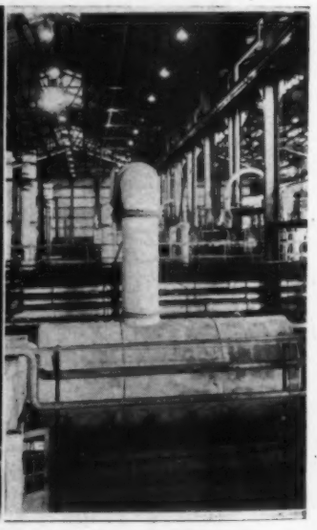


Overhead view of portion of the plant

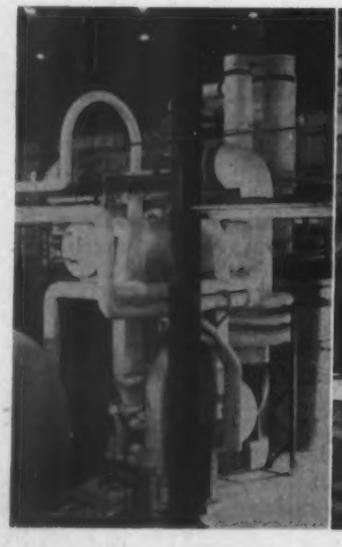
Air preheater

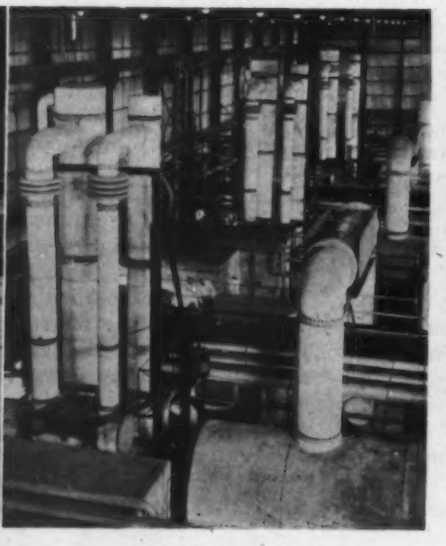


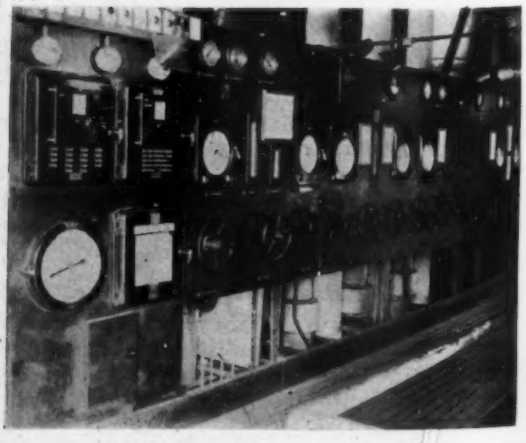
Secondary reformer



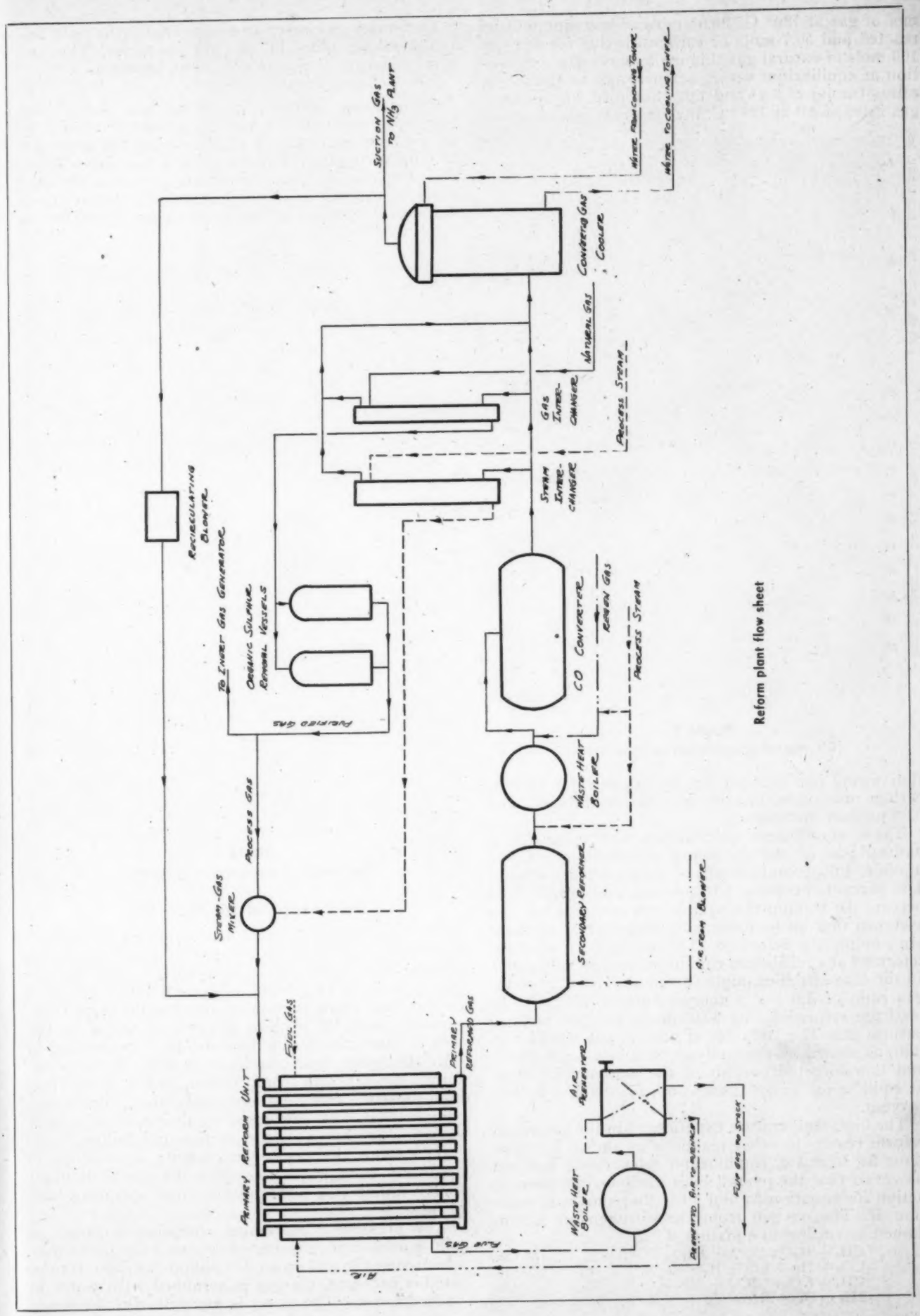
CO converter







Left: Waste heat boiler. Center: Gas and steam interchangers. Above: Control panel board.



Reform plant flow sheet

mol of gas at 720° C., 90.65 mols of methane will be reacted and 50.7 mols of carbon dioxide formed per 100 mols of natural gas. Figure 4 shows gas composition at equilibrium versus temperature at steam/gas ratios (mols) of 3.24 and 4.0. Therefore, for a steam/gas ratio of 4.0 at 720° C. the reformed gas composi-

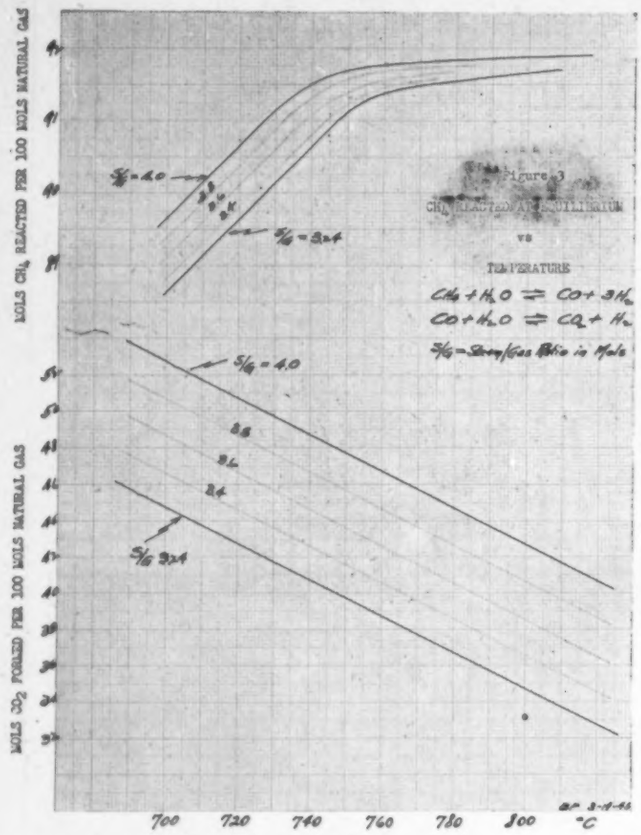


FIGURE 3
CH_4 reacted at equilibrium vs. temperature

tion would be: 76.7 percent hydrogen, 11.7 percent carbon monoxide, 11.2 percent carbon dioxide, and 0.32 percent methane.

These equilibrium calculations are made for a natural gas of the following composition: carbon dioxide, 1.6 percent; methane, 92.2 percent; ethane, 4.62 percent; propane, 1.16 percent, and butane, 0.42 percent. In making the equilibrium calculations, it is assumed that all hydrocarbons higher than methane are completely reformed. The amount of methane reformed at equilibrium conditions is then calculated. In the case of the example shown above for a steam/gas ratio of 4.0 and a temperature of 720° C., the methane reformed was 90.65 mols per 100 mols of natural gas. The 100 mols of natural gas would contain, as shown by the analysis, 92.2 mols of methane and therefore the percent of the methane reformed at equilibrium under these conditions would be 98.3 percent.

The high temperature experienced in the secondary reform results in other reactions as shown by equations 5a, b, and c. Equilibrium calculations indicate, however, that the overall hydrocarbon reforming reaction for equation 5a and 5b is that shown in equation 5c. The oxygen from the nitrogen air is consumed according to equation 6.

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad (5a)$$
$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad (5b)$$
$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \quad (5c)$$
$$2H_2 + O_2 \rightleftharpoons 2H_2O \quad (6)$$

The water gas reaction is essentially the only reaction taking place in the CO converter. This reaction, shown in equation 7, is exothermic.

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (7)$$

Aside from temperature, steam/gas ratio, and partial pressure of the reactants, space velocity is another important factor in calculating the expected activity of a catalyst in promoting the above mentioned reactions. Space velocity is known as the volumes of gas per hour per volume of catalyst. Low space velocities favor the reaction going nearer to equilibrium.

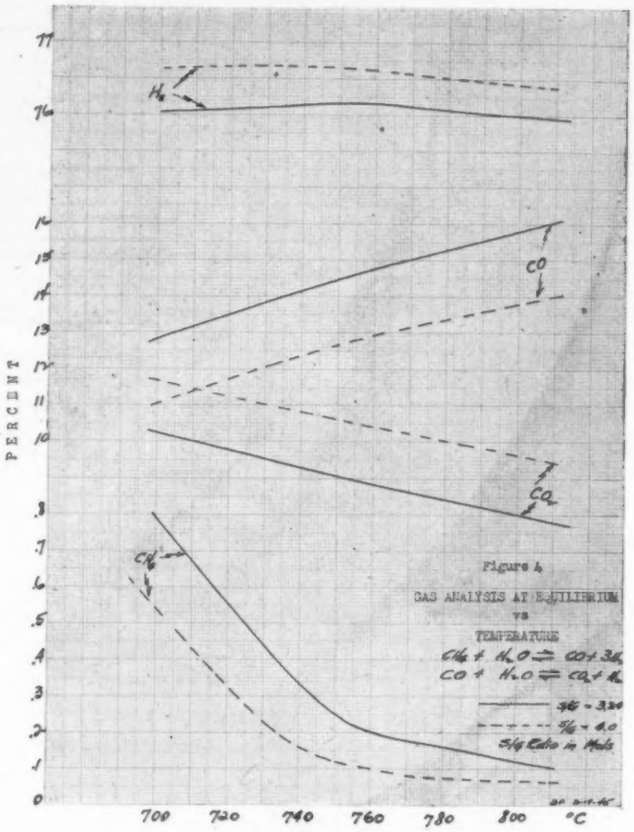


FIGURE 4
Gas analysis at equilibrium vs. temperature

Purification of the Raw Gas

The suction gas contains approximately 20 percent impurities. The greater portion of these is carbon dioxide with some carbon monoxide, a trace of oxygen, and about 1.2 percent total inerts. This gas goes to the first stage suction of the low-pressure compressors with the suction gas holder riding on the line to take care of fluctuations. It is interesting to note that very close coordination exists between reform, low-pressure compression, water scrubbing, high-pressure compression, purification, sixth-stage compression, and synthesis, so that normally little variation is shown in the suction gas holder level. Furthermore, the gas holder capacity is sufficient to hold only enough gas to supply the synthesis plant for 10 minutes or less under normal operating conditions.

Low-pressure compression comprises a group of 1000-horsepower gas-engine-driven compressors which step the gas up to 230 pounds in three stages. At this pressure, the gas is scrubbed with water in packed towers. The water is pumped over the tower

Fifty-four-inch process gas line from reform plant. Gas holder in background

by means of centrifugal pumps driven by 1000-horsepower gas engines. The water from the towers is let down through a water wheel connected to an electric generator for recovery of some of the power. From the let-down the water goes to the degasifying tower for removal of absorbed gases and cooling. The water from the degasifying tower shows a residual CO_2 of 20 to 50 parts per million and is picked up by the pump for recirculation through the water scrubber.

The next step in the purification is the removal of carbon monoxide, oxygen, and the remaining carbon dioxide. This is accomplished by scrubbing the gas with copper liquor and caustic in a manner similar to that mentioned with the Haber-Bosch process.

The gas exit the water scrubbers enters the fourth-stage suction of the high-pressure compressors. These are driven by 1000-horsepower gas engines. The fourth and fifth stages step the gas up to 1800 to 1900 pounds at which pressure it is sent to the copper scrubbers. These scrubbers are nearly 60 feet high and at temperatures of 0-15° C. (32-59° F.), the copper liquor scrubs the gas and removes the carbon monoxide (down to 10 to 20 ppm), all the oxygen, and most of the carbon dioxide. The gas then passes to a smaller caustic scrubber and is scrubbed with a weak caustic soda solution resulting in an exit gas containing only 0 to 5 ppm carbon dioxide. This then concludes the purification step with the exception of the regeneration phase in connection with the copper liquor.

The cool copper liquor from the scrubber enters the top of the regenerator and serves as a reflux to scrub excess ammonia from the regen gas. The liquor then flows to the regeneration section where carbon monoxide and dioxide are liberated at temperatures of aproximately 75° C. (167° F.). Ammonia and air are introduced in the regenerator for control of free ammonia and cupric concentration of the copper liquor. These act as stabilizing agents for the copper liquor. Low ammonia content will result in precipitation of copper oxide, while low cupric will result in precipitation of metallic copper. Furthermore, only the cuprous copper compounds absorb the carbon monoxide so that cupric copper in excess of that required for stabilizing the solution replaces cuprous copper and decreases the scrubbing capacity of the solution.

The chemistry of the copper and caustic purification is shown by the equations given below. The copper liquor is a complex mixture of cuprous ammonium formate and carbonate, cupric ammonium formate and carbonate, ammonium carbonate, and ammonium hydroxide. The following equations are given to show the various reactions involved in the scrubbing and regeneration operations:

$$\underset{\text{Cuprous Ammonium Formate}}{\left[\begin{matrix}NH_3\\ NH_3\ Cu\ NH_3\\ NH_3\end{matrix}\right]}COOH + CO \rightleftharpoons \left[\begin{matrix}NH_3\\ NH_3\ Cu\ NH_3\\ NH_3\end{matrix}\right]COOH \cdot CO \qquad (8a)$$

$$\underset{\text{Cuprous Ammonium Carbonate}}{\left[\begin{matrix}NH_3\\ NH_3\ Cu\ NH_3\\ NH_3\end{matrix}\right]_2}CO_2 + 2CO \rightleftharpoons \left[\begin{matrix}NH_3\\ NH_3\ Cu\ NH_3\\ NH_3\end{matrix}\right]_2 CO_2 \cdot 2CO \qquad (8b)$$

$$2\underset{\text{Cuprous Ammonium Formate}}{\left[\begin{matrix}NH_3\\ NH_3\ Cu\ NH_3\\ NH_3\end{matrix}\right]}COOH + CO + O_2 \rightleftharpoons$$

$$\underset{\text{Cupric Ammonium Formate}}{\left[\begin{matrix}NH_3\\ NH_3\ Cu\ NH_3\\ NH_3\end{matrix}\right]}(COOH)_2 + \underset{\text{Cupric Ammonium Carbonate}}{\left[\begin{matrix}NH_3\\ NH_3\ Cu\ NH_3\\ NH_3\end{matrix}\right]}CO_3 \qquad (9a)$$

$$\underset{\text{Cuprous Ammonium Carbonate}}{\left[\begin{matrix}NH_3\\ NH_3\ Cu\ NH_3\\ NH_3\end{matrix}\right]_2}CO_2 + CO + O_2 \rightleftharpoons 2\underset{\text{Cupric Ammonium Carbonate}}{\left[\begin{matrix}NH_3\\ NH_3\ Cu\ NH_3\\ NH_3\end{matrix}\right]}CO_3 \qquad (9b)$$

$$2NH_3 + H_2O + CO_2 \rightleftharpoons \underset{\text{Ammonium Carbonate}}{(NH_4)_2CO_3} \qquad (10)$$

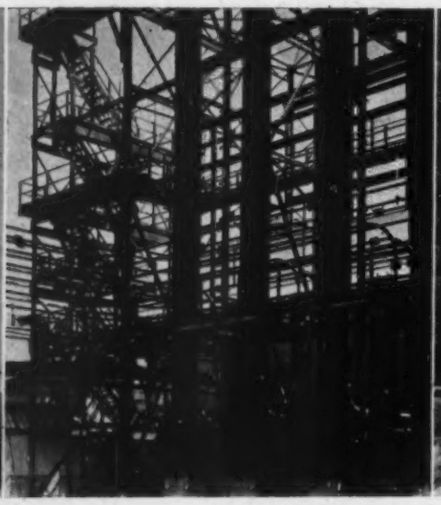
The absorption of the CO and CO_2 is shown by

Ammonia Plant

(Location of these views may be identified on opposite flow chart)

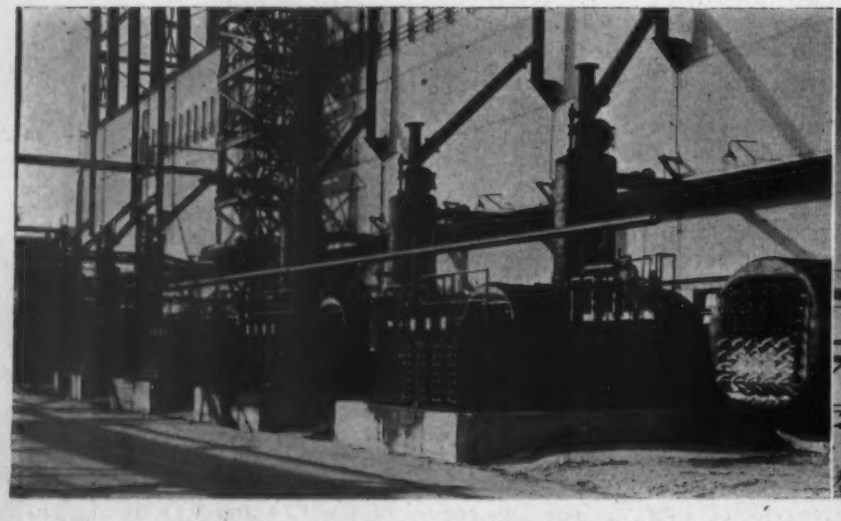
Process gas compressors: High-pressure, left; Low-pressure, right

Water scrubbers

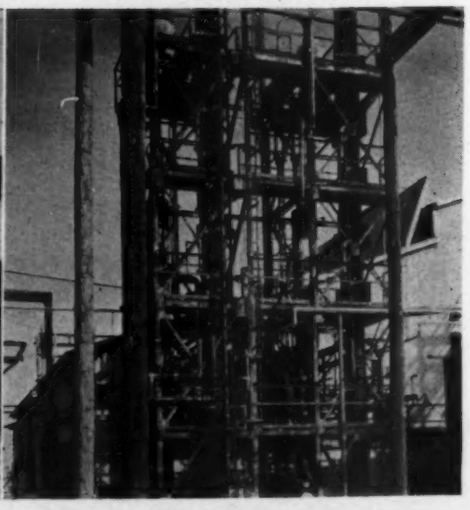


Copper and caustic scrubbers

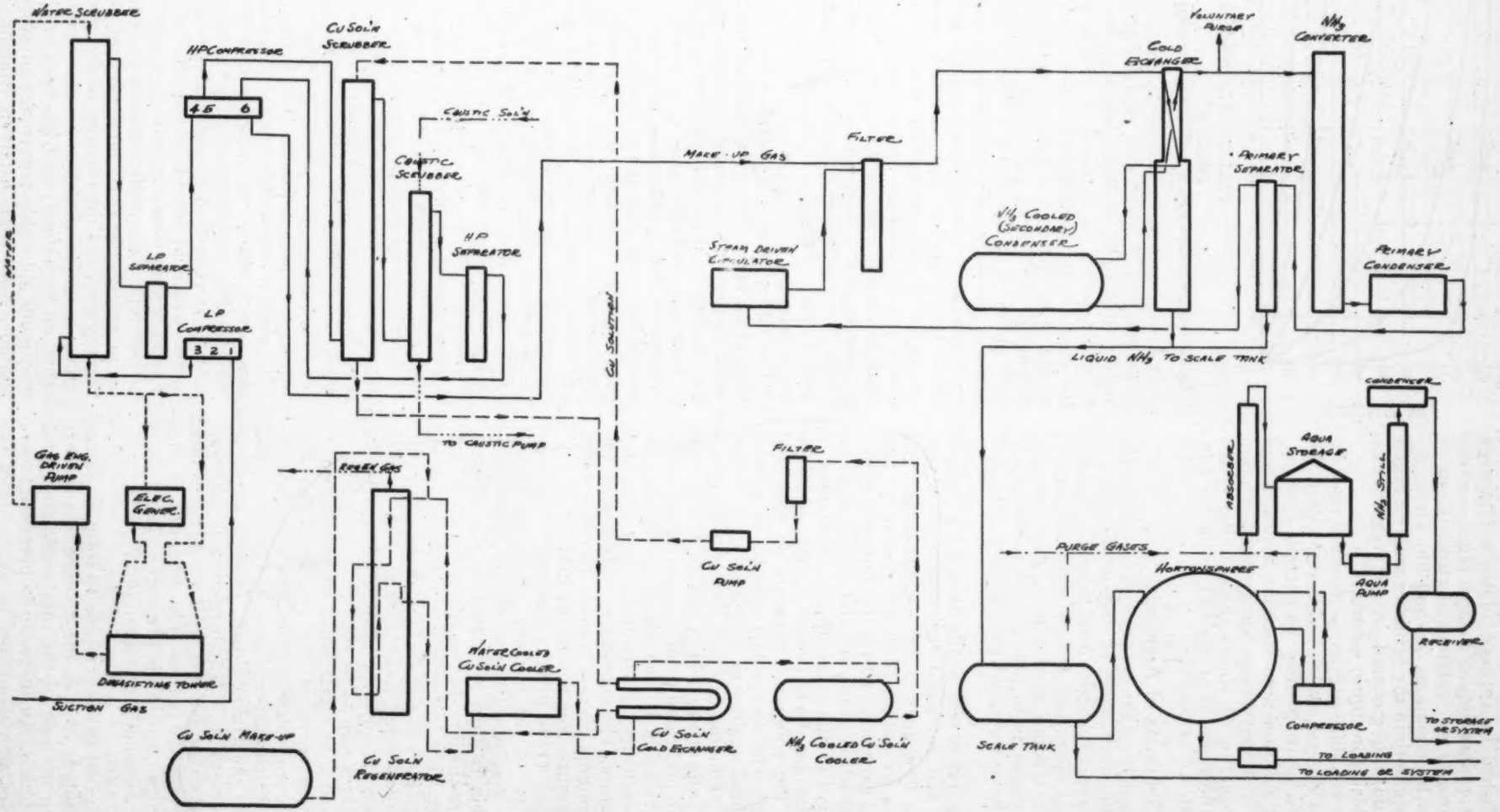
Copper solution coolers



Primary and secondary condensers for ammonia synthesis



Absorbers and stills



Ammonia plant flow sheet

equations 8a, 8b, and 10. Regeneration of the solution is accomplished by reversal of these reactions on heating the copper liquor in the regen section of the regenerator. The oxidation of cuprous ion to cupric is shown by equations 9a, and 9b. These reactions take place both in the scrubber where oxygen is removed from the gas and in the regenerator where air is added for cupric control.

The caustic scrubbing solution is used for removal of the CO_2 from the gas, and is recirculated until the solution reaches approximately 80 percent carbonation. The spent solution then contains hydrates and carbonates, the hydrate content being only a fraction of a percent. Equation 11 shows the reaction which takes place in the removal of the CO_2 from the gas.

$$2NaOH + CO_2 = Na_2CO_3 + H_2O \qquad (11)$$

Synthesis of Ammonia

The purified gas from the copper and caustic scrubbers goes to the sixth stage of compression and is discharged at approximately 5000 pounds pressure for the synthesis operation. It is of extreme importance that the gas going to synthesis, make-up gas, be of high purity so as to prevent the formation of carbamate in the system and poisoning of the catalyst.

The make-up gas enters at the filter with the gas being recycled and entrained compressor oil is separated. The gas then goes to the cold exchanger and from thence to an ammonia-cooled condenser and back to the cold exchanger where the ammonia which has been condensed is drawn off and sent to storage. Final purification of the make-up gas is attained in this vessel. The gas then passes to the ammonia converter and the voluntary purge is on this converter inlet line. The ammonia converter is a combination of a heat exchanger and a catalyst basket containing the ammonia catalyst. The reaction takes place at high temperature, 500° C. (932° F.), so that the gas must be preheated prior to entering the catalyst bed. The reaction is also highly exothermic so that the heat exchanger serves to prevent excessive rise in temperature. The conversion of hydrogen and nitrogen to ammonia gives a volume decrease which results in a pressure drop across the unit.

The hot gases (130-140° C.) (266-284° F.) from the converter go to the primary condenser (water cooled) where a substantial part of the ammonia is condensed. This is then separated in the primary separator where the liquid ammonia is drawn off and sent to storage. The re-cycle gas containing some ammonia vapor goes to the suction of the circulator. Here it is recompressed from 4500 to 5000 pounds for recirculation through the system and enters the filter with the make-up as heretofore mentioned.

It is interesting to relate some of the chemistry and development work of the synthetic ammonia process. The process described herein is an adaptation of the American process and shows a great deal of similarity to the Haber-Bosch. In such synthetic ammonia processes a 3:1 hydrogen and nitrogen mixture is brought in contact with a substance such as specially prepared porous iron granules at elevated temperature and high pressure. These gases unite to form ammonia, equation 12.

$$3H_2 + N_2 \rightleftharpoons 2NH_3 \qquad (12)$$

The two original gases combine to form a minute amount of ammonia even in the absence of a contact substance. The purpose of the catalyst is merely to hasten the reaction. An increase in pressure favors the formation of ammonia, since as we see from the reaction given in the above equation, four volumes

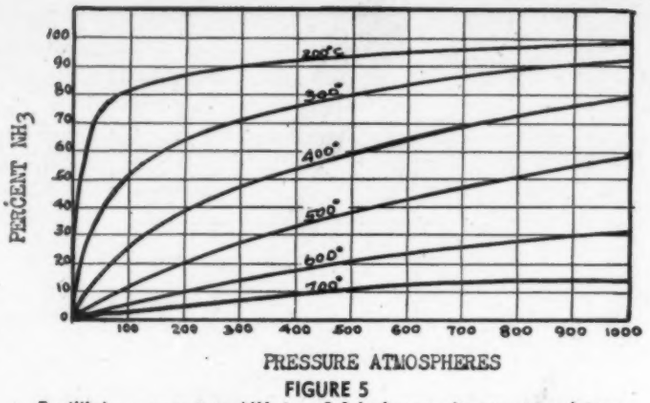


FIGURE 5
Equilibrium percentage NH_3 in a 3:1 hydrogen-nitrogen gas mixture

of the original gases combine to form two volumes of ammonia. It is necessary that the temperature be high enough to allow high activity. However, beyond a certain point, an increase in temperature retards the reaction by favoring the decomposition of ammonia. The chart in Figure 5, as given in "Fixed Nitrogen" by Curtis and taken from experimental data obtained at the Fixed Nitrogen Research Laboratory, gives curves for equilibrium percentages of ammonia at various temperatures and pressures. From this chart we see that for a pressure of 350 atmospheres and a temperature of 500° C. we would reach a concentration of 30 percent ammonia at equilibrium. It will be noted that the lower temperatures show a higher percent ammonia at equilibrium, but the higher reaction temperatures such as 500° C. are used since the speed of the reaction is much faster.

The effect of inerts (methane and argon) is that they build up in the cycle gas and the partial pressures of the hydrogen and nitrogen are thereby reduced. The total partial pressure of the 3:1 mixture of hydrogen and nitrogen is, of course, the reaction pressure in the synthesis of ammonia. Therefore, it should be noted that either hydrogen or nitrogen in excess of the 3:1 ratio serve to reduce the partial pressure of the reactants the same as the inert gases and close control of the 3:1 ratio is important. Inert content of the converter inlet gas may vary from 15 to 25 percent according to operating conditions.

The common type of catalyst used is that known as a promoted iron catalyst. With the American system, the catalyst consists of iron-oxide Fe_3O_4 granules containing approximately 1 percent potassium oxide and 3 percent aluminum oxide. The catalyst is prepared by burning pure iron in oxygen. The oxide is fused in an electric furnace, the promoters added, the mass cooled, crushed, and then screened to the desired mesh. This material is placed in the converter and the hydrogen of the regular hydrogen-nitrogen mixture is used to reduce the iron oxide to the metal. This process apparently results in porous iron granules which means the development of considerable surface. The promoter effect of potassium oxide is said to be restricted to use with another oxide promoter which is irreducible or difficultly reducible. The aluminum oxide appears to be the principle one of this type. One explanation of the beneficial effect of promoters is that they prevent sintering and thereby preserve the porosity of the catalyst.

One manufacturer of ammonia catalyst puts much stress on high purity and has very low limits on the maximum allowable percentage of phosphorous and sulphur. Also, some catalysts contain approximately one percent aluminum oxide and 1.8 percent potassium

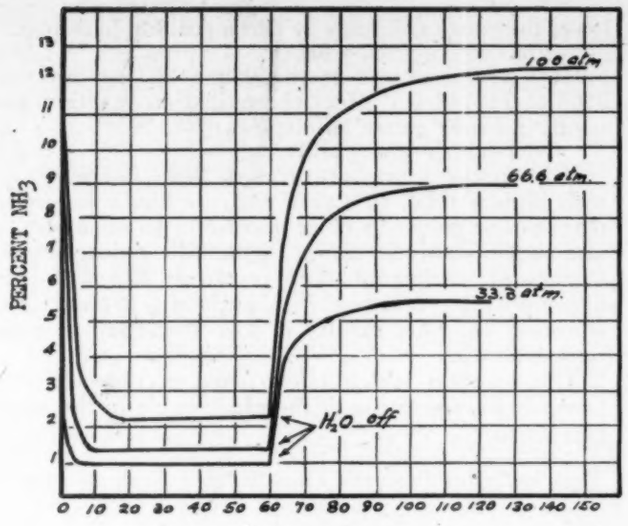


FIGURE 6
Poisoning effect of 0.32 percent H_2O vapor on the activity of a doubly promoted ammonia catalyst at high pressure.

oxide, which is a somewhat different ratio of these constituents than is shown above.

It is difficult commercially to remove the last traces of poison from the make-up gas. The chief offenders among these poisons are water vapor, carbon monoxide, and carbon dioxide, all of which Curtis classifies as temporary poisons. The presence of these poisons in quantities as low as 0.1 percent or less can temporarily destroy the activity of the catalyst and "knock out" a converter in a very few minutes. Such incidents can easily result in down time of 24 hours duration for a converter. The importance of gas purity cannot be over-emphasized. The chart shown in Figure 6, taken from Curtis, illustrates the detrimental effect of a poison. The curves are somewhat misleading, however, in that converters "knocked out" by poisonous gas particularly in the case of carbon monoxide and carbon dioxide, are not usually brought back on the line as readily as the curves seem to indicate they might be.

Recovery of Ammonia

The ammonia storage, recovery, and loading are all located in the same area. Here the anhydrous ammonia from the primary and secondary separators is received through a common line into scale tanks. The production is weighed and then transferred to storage or loaded direct into tank cars. Scale tank pressure is approximately 200 pounds.

The storage tanks are spheres with a capacity of approximately 500 tons each. Compressor units are provided for recompression of the vapors from the spheres so that the ammonia in the spheres may be held at 65 pounds pressure. Non-condensable gases are purged off of the compressor system and condensed ammonia returned to the spheres. These non-condensable gases are hydrogen, nitrogen, methane, and argon which have been dissolved in the liquid ammonia at the high pressure of the synthesis system. Ammonia storage includes two distribution tanks for nitric and ammonium nitrate plant use.

The recovery units consist of an absorber and ammonia still. The gases charged to the absorber consist of a mixture of the purges from scale tanks, distribution tanks, and tank cars during loading. This purge gas is scrubbed with water in the absorber with a resulting aqua of approximately 22 percent ammonia on one pass. The aqua goes to storage tanks from which it is charged to the ammonia still.

The aqua is charged to a combination bubble tower and still which operates at 200 pounds pressure with a temperature gradient of 40° C. (104° F.) at the top and 200° C. (392° F.) at the bottom. Open steam is used as the source of heat in the bottom of the still. The vapors from the still go to an overhead condenser. Part of the condensed ammonia returns to the tower as reflux and the remainder goes to the ammonia receivers. The still is designed to produce ammonia with 0.2 percent water, and it operates with a water content near this figure.

Ammonia Oxidation for the Manufacture of Nitric Acid

The principal steps in the manufacture of nitric acid by ammonia oxidation are the burning, secondary oxidation, and absorption of the nitrogen oxides. The raw materials used are anhydrous ammonia, compressed air, and distilled water. The latter should be of high purity and particularly should be low in chlorides. The nitric acid equipment is made of stainless steel and the system operates at 60 pounds pressure.

Purified air for the process is split into three streams, one going to the air preheater, another to the mixer filter, and the other (secondary air) to the bleacher and thence to the oxidation tower. Ammonia of high purity comes from an ammonia evaporator at approximately 50° C. (122° F.) and is mixed with air at the mixer filter. These streams are so regulated that a mixture of 9-10 percent ammonia is fed to the burner at 280 to 300° C. (536 to 572° F.). Higher temperature may bring about thermal decomposition of the ammonia. The mixture is passed over the catalyst, a platinum alloy gauze, and here, once ignited, the stream of ammonia continues to burn. The temperature is held near 900° C. (1652° F.), and the ammonia burns to nitrogen oxide. The reaction is highly exothermic.

The hot gases pass to a waste-heat boiler and then to a condenser. From here, the gases go to the oxidation tower where the principal oxidation of the NO to NO_2 takes place. This secondary oxidation is begun in this tower and must be continued throughout the absorption system as will be shown later. Air from the bleacher is utilized for the secondary oxidation.

From the oxidation tower the oxidized gases pass to a series of towers comprising the absorption system. Excess oxygen is maintained throughout the system, and the tail gas leaving the top of the No. 1 tower in the system contains 2 to 3 percent oxygen and approximately 0.2 percent nitrogen oxides. Condensate for the absorption of the nitrogen dioxide to form nitric acid is introduced at the top of the No. 1 tower. Heat is developed as the nitrogen dioxide is absorbed, and since the absorption is more complete at low temperatures the acid is recirculated through each tower with a cooling coil in each circulating system. A portion of the stream is continually fed to the next tower. The acid from the last absorption tower goes to the bleacher which is blown with air to strip out nitrous gases. The air from the bleacher, as mentioned above, is the secondary air which is fed to the oxidation tower.

The bleacher acid is normally water white and has a strength of approximately 56 percent nitric acid. Higher-strength acid may, however, be made in pressure absorption systems such as this one.

The chemistry of the ammonia oxidation process is shown by the equation given below. The ammonia-

air mixture passed through a red hot, fine mesh, platinum gauze gives the following overall reaction:

$$4NH_3 + 5O_2 = 4NO + 6H_2O \quad (13)$$

(Nitric Oxide)

The temperature of burning is controlled by proper regulation of the ammonia concentration, preheat temperature, and the velocity of the gas stream. Conversions of 95 percent and higher are not uncommon. The standard procedure is to use gauze of 80 mesh, and the time of contact is of the order of 0.0014 second, in which time reaction 13 has reached completion. This time, it may be noted, is a much shorter contact time than is experienced with most catalytic reactions.

Where ammonia is allowed to pass through the gauze due to excessive velocities or cold spots on the gauze, the following reaction may take place and lower the gauze efficiency by decomposition to nitrogen:

$$4NH_3 + 6NO = 5N_2 + 6H_2O \quad (14)$$

High temperatures at the gauze on the order of 970° C. (1778° F.) effect the oxidation reaction and result in lower gauze efficiencies:

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O \quad (15)$$

High preheat temperatures of 350° C. (662° F.) and higher tend to cause the ammonia before it reaches the gauze to react according to equation 13, due to the catalytic action of metallic oxides on the surface of equipment. The resulting NO will then decompose by reacting with ammonia according to equation 14. This results in low efficiency as mentioned above.

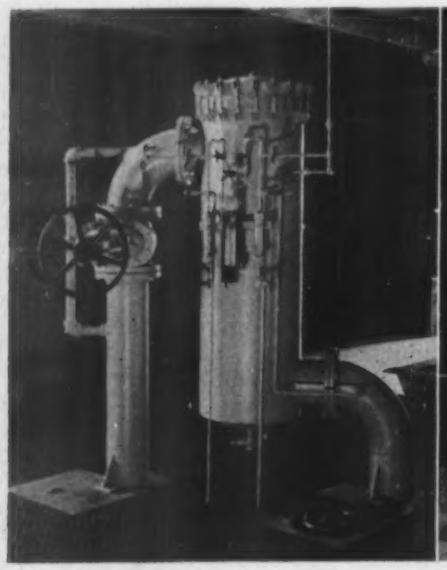
The reaction which takes place in the oxidation tower is the oxidation of the nitric oxide to the nitrogen dioxide.

$$2NO + O_2 = 2NO_2 \quad (16)$$

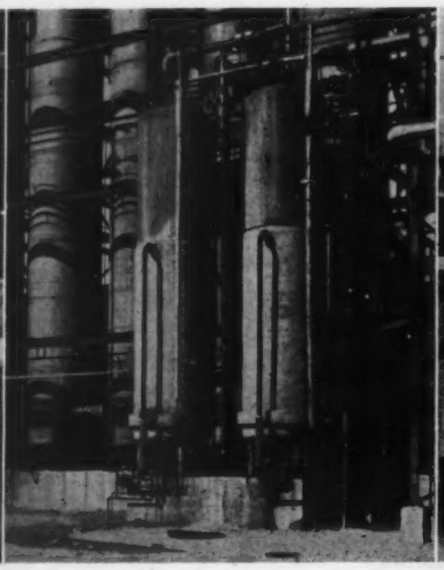
This reaction requires considerable time so that it

Ammonium Nitrate Plant

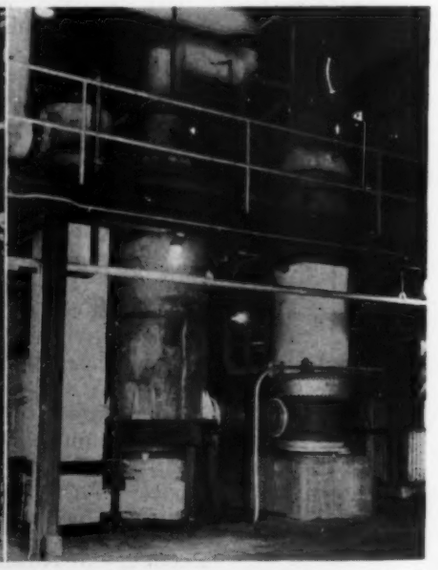
(Location of these views may be identified on opposite flow chart)



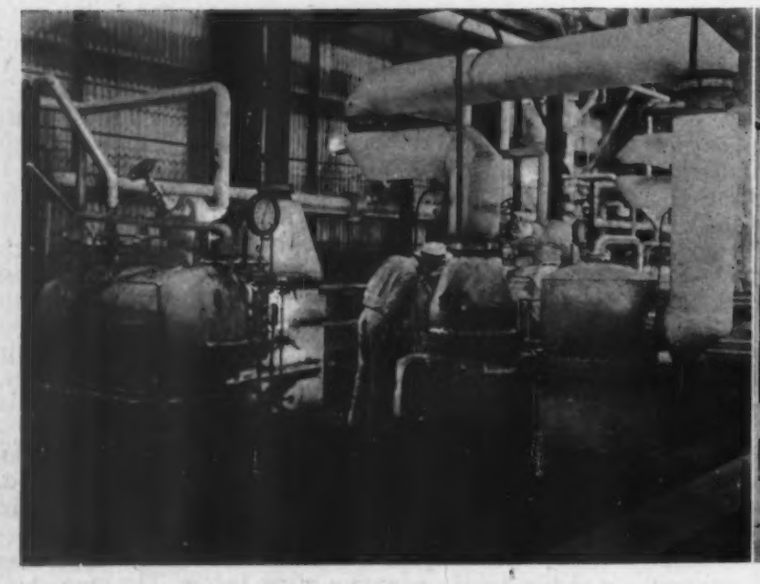
Air filter



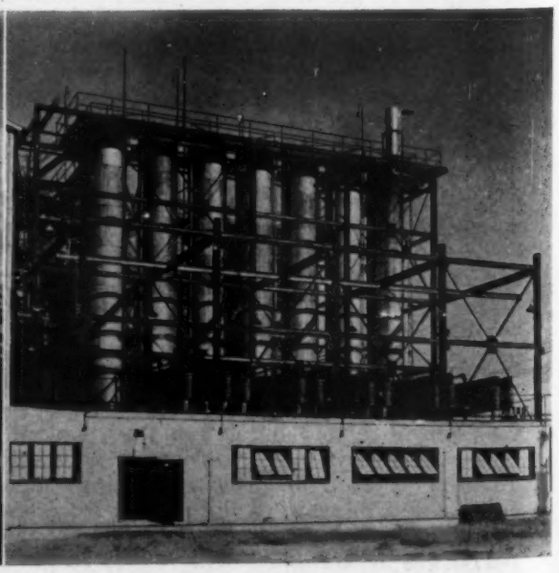
Ammonia evaporators



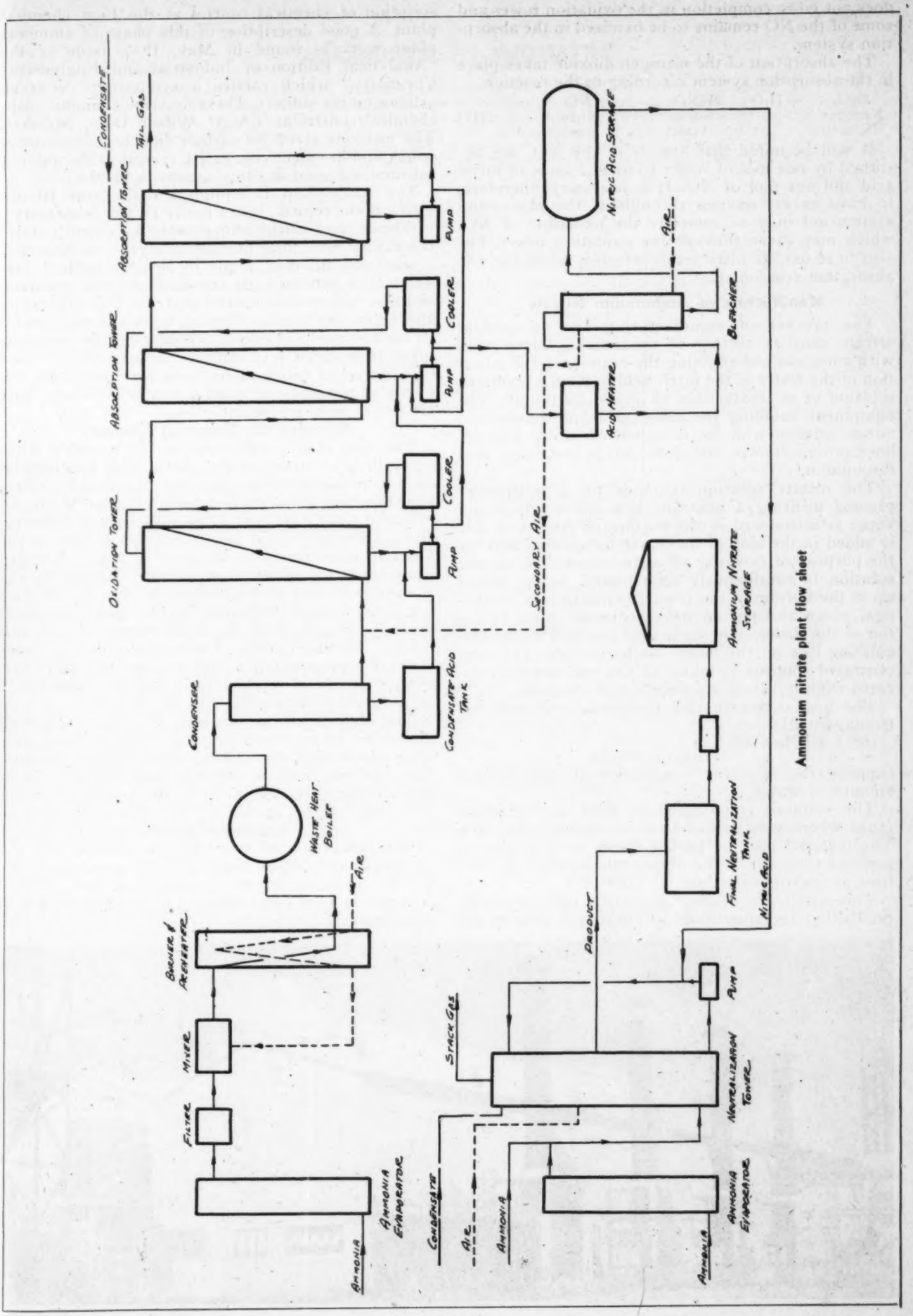
Mixer filter; burner-pre-heater; waste heat boiler.



Gauze is periodically inspected through burner porthole



Absorbers and trickle coolers



Ammonium nitrate plant flow sheet

does not go to completion in the oxidation tower and some of the NO remains to be oxidized in the absorption system.

The absorption of the nitrogen dioxide takes place in the absorption system according to the reaction:

$$\underset{\text{Nitrogen Dioxide}}{3NO_2} + H_2O = \underset{\text{Nitric Acid}}{2HNO_3} + \underset{\text{Nitric Oxide}}{NO} \qquad (17)$$

It will be noted that 3 mols of the NO_2 are absorbed by one mol of water to form 2 mols of nitric acid and one mol of NO. It is necessary, therefore, to have excess oxygen throughout the absorption system not only to complete the oxidation of NO, which may carry through the oxidation tower, but also to re-oxidize nitric oxide which is formed in the absorption reaction 17.

Manufacture of Ammonium Nitrate

The process of manufacturing the ammonium nitrate consists merely of neutralizing nitric acid with ammonia and effecting the evaporation of a portion of the water in the nitric acid to form a resultant solution of approximately 82 percent strength. The equipment handling the nitric acid and ammonium nitrate solution with the exception of nitrate transfer lines, process storage, and plant storage is stainless steel throughout.

The nitrate solution is made by a continuous process utilizing a neutralization tower. Ammonia vapor is introduced in the bottom of the tower. Air is added in the side of the tower for cooling and for the purpose of carrying off water vapor. The nitrate solution is continuously recirculated, being picked up at the bottom of the tower by means of a centrifugal pump and put on the distribution plate in the top of the tower. The nitric acid is added to the circulating line on the pump discharge side. The concentrated solution is taken off the product plate located slightly below the middle of the tower.

The heat of reaction of the nitric acid and ammonia, equation 18,

$$HNO_3 + NH_3 = \underset{\text{Ammonium Nitrate}}{NH_4NO_3} \qquad (18)$$

supplies the heat for evaporation of the desired amount of water.

The solution is collected in final neutralization tanks where it is adjusted to the desired alkalinity. The material may be loaded direct to tank cars or pumped to storage. The 82 percent solution crystallizes at approximately 65° C. (149° F.).

This article is dealing primarily with ammonia production and space does not permit a detailed description of chemical control at the Lion chemical plant. A good description of this phase of ammonia plant work is found in May, 1945, issue of the "Analytical Edition of Industrial and Engineering Chemistry" which carries a symposium of seven articles on the subject. These describe ammonia plant chemical control at T.V.A., Wilson Dam, Alabama. The methods given for carbon dioxide, carbon monoxide, and bi-valent copper are typical of the analytical methods used at other ammonia plants.

The Lion plant is equipped with plant laboratories at the reform, boiler house (water laboratory), synthesis, and nitric acid plants. A central control laboratory runs final product analyses, oil analyses, natural-gas analyses, argon by density method, prepares all solutions both standard and non-standard, and also runs various special analyses. This laboratory also takes care of glass blowing work and supplies for all laboratories. The chemical control for the ammonia plant is more or less centered around the CO and CO_2 electrical conductivity tests for controlling the purity of the make-up gas for synthesis. These tests are felt to be of major importance.

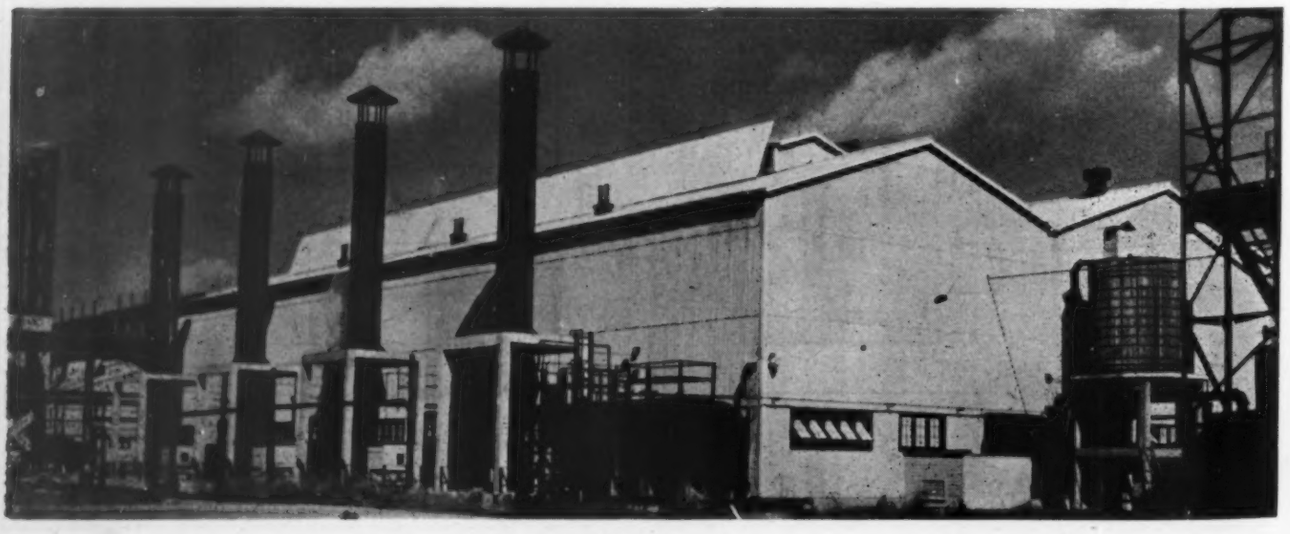
Nitrogen the Essential Element

The story of ammonia would not be complete without calling to attention the varied uses and importance to mankind of the nitrogen compounds. Nitrogen, the inert element, is a basic element of life, an essential plant food, and a key substance of industry. Half of Europe's food and 15 percent of that in the United States traces to fertilizer of which nitrogen compounds are vital constituents. Nitrogen is the essential element in explosives, so that in the past few years a large portion of the nitrogen compounds produced was used for the manufacture of such materials. The distribution of nitrogen in normal peace times is approximately as follows: agriculture 75 percent, commercial explosives 7 percent, chemical 6 percent, other industrial uses 12 percent.

The importance of nitrogen in industry is well illustrated by an accompanying chart, showing how ammonia is used throughout the various industries. Nitrogen may well be called an essential element of industry since its use is certainly varied and extensive, as is clearly shown by the chart.

Acknowledgment

The author wishes to gratefully acknowledge the assistance and helpful suggestions of members of the technical and supervisory personnel of the Chemical Division of Lion Oil Company in the preparation of this article.



Boiler house

AMMONIA IN INDUSTRY

Agriculture

Anhydrous ammonia, aqua ammonia, ammoniated phosphates, ammonium nitrate solution, grained ammonium nitrate, sodium nitrate (derived from nitric acid or nitrous gases made by ammonia oxidation) supply nitrogen which is one of the essential elements for plant growth. Ammonia may be combined with carbon dioxide to form urea. Urea and urea-ammonia-nitrate solutions are used as fertilizers. Urea is used as a cattle feed. Ammonium sulfamate is finding wide use as a weed killer. Dissociated ammonia may serve as a source of hydrogen in the hydrogenation of cotton seed oil.

Chemicals

Ammonia is used in the production of nitric acid by oxidation. Nitric acid is used in organic synthesis for the production of nitrobenzol, nitroparaffins, and many other nitro compounds. Also in the production of amines. Ammonia is used to furnish nitrogen oxides in the production of sulphuric acid by the chamber process. It is utilized in the manufacture of caustic soda by the Solvay process. Ammonia is used in the production of amines by aminolysis in organic synthesis. Ammonia, the amines, and nitro compounds are used as reaction mediums and solvents in the chemical industry.

Explosives

Ammonia oxidation is the chief source of nitric acid. Ammonia and nitric acid form the base for explosives. Nitric acid is the nitrating agent for the manufacture of nitroglycerine from glycerin, TNT from toluene, picric acid from phenol, and nitrocellulose from cellulose. RDX explosive is made by reacting ammonia with formaldehyde and nitrating the resulting product. Ammonium nitrate is used in the manufacture of amatol. Smokeless powder is made by the nitration of cellulose.

Metallurgy

Certain metals such as copper, nickel, and molybdenum may be extracted from their ores by the use of ammonia. Ammonia is used as a nitriding agent for certain types of alloy steels. Ammonia is dissociated into its elements, and the resulting gases used as a protective coating for bright annealing, powder metallury, and brazing. Dissociated ammonia also serves as a source of hydrogen for welding and in the production of metal powders.

Petroleum

Ammonia is used to neutralize acid constituents of treated petroleum oils. It is used to protect equipment from corrosion by acid products. Dissociated ammonia may be used in hydrogenation of petroleum fractions. It is used for refrigeration in dewaxing and other operations. Ammonia is used in copper ammonium solutions for purification of unsaturated compounds.

Pharmaceuticals

Ammonium acetate, ammonium benzoate, ammonium bromide, ammonium camphorate, ammonium citrate, ammonium glycerophosphate, ammonium iodide, ammonium salicylate, and ammonium urate are all used in the drug and medical field.

Plastics

Ammonia may be combined with carbon dioxide to form urea. Urea is utilized in the manufacture of urea-formaldehyde resins and urea-furfural resins which are important plastics. Urea and formaldehyde are combined to form dimethylol urea. Urea is used in plastic wood and dimethylol urea in transmuted wood. Ammonia is used as a catalytic agent in the production of several plastics such as the Phenol-formaldehyde type. It is used as a coagulent in the manufacture of casein plastics. Celluloid, Pyroline, Viscoloid, and Fiberloid are made from nitrocellulose and are thus indirectly dependent on ammonia.

Refrigeration

Ammonia is one of the oldest refrigerants known. Favorable prices such as prevail at present should result in more extensive use of ammonia as a refrigerant. Ammonia is used in both absorption and compression refrigerating systems. It is widely used in refrigeratings systems for ice plants, food lockers, cold storage, and various industrial processes.

Rubber

Ammonium soaps form a polymerizing medium for styrene. Ammonium chloride is one of the reagents in the production of chlorobutadiene. Ammonium hydroxide is used in the manufacture of polychloroprene. Ammonium chloride is used in producing vinylacetylene from acetylene. Vinylacetylene is used in the manufacture of butadiene. Copper ammonium salts are used in the purification of butadiene.

Textiles

Ammonolysis such as the reaction of benzene and ammonia furnishes aniline and other amines which is the base for many dyes and dyestuff intermediates. Ammonia is used in the production of cuprammonium rayon. Ammonia is used catalytically in the preparation of hexamethylene diamine from adipic acid. Hexamethylene diamine is one of the two major raw materials used in the production of nylon. Ammonia is utilized in the manufacture of scouring agents for textiles.

Micellaneous

Ammonia is used in conjunction with chlorine for the purification of water supplies. It is used as a nutrient for yeast in the production of industrial alcohol. Ammonium borate is used as a fireproofing agent for wood and textiles. Ammonium bifluoride is used in glass etching and as a germicide in the food and dairy industries. Ammonium chloride is used in the manufacture of dry cell batteries.

Group of pipefitters being shown proper technique in opening pipe lines. Note that the demonstration equipment is under pressure to simulate actual conditions.

Planned Yard Conferences Enlist Workers in Maintaining

Baton Rouge Refinery's Good Safety Record

ARTHUR J. FERGUSON, Safety Engineer
Standard Oil Company of New Jersey, Louisiana Division

THE oil refinery operated by Standard Oil Company of New Jersey at Baton Rouge, Louisiana, underwent expansion in recent years, resulting in the increasing of its personnel from about 4000 workers in the prewar period to a total of better than 8000 at this time. This great expansion of personnel and facilities brought with it many new and varied safety problems. It soon became apparent that some extensive program would be necessary to cope with these new safety problems and maintain the level of safety that existed in the refinery in prewar years.

One of the main problems of accident prevention at the refinery centers around the Mechanical Department, consisting of some 3500 workers who handle practically all maintenance and a good part of the construction work in the refinery. This group is made up of pipefitters, boilermakers, machinists, masons, carpenters, painters, and other mechanical crafts, along with general laborers. It soon became apparent that the primary need of this group was planned training in the safety phases of their work. This training was required by both the supervisors and the rank and file. After considerable study, it was decided that the most effective means for carrying out this training need would be through arranging safety educational classes for the various crafts, having in attendance at any one class only one gang or group of men that normally work together. Following this plan, the classes were limited in size to 10 to 15 men.

A review of the accident experience records showed that the two most prominent causes of injury were opening equipment and handling materials. The first factor concerns primarily the pipefitters and machinists; however, the second factor was a problem of all of the crafts. Arrangements were accordingly made to have safety-educational classes presented with these two considerations as the principal subjects.

Equipment Opening

For the equipment-opening class, a pipe demonstration piece was fabricated, consisting of a vertical section of 4-inch pipe mounted on a stand and having at its center a pair of flanges which permitted opening

the line. A connection was provided at the bottom of the pipe section to permit applying water pressure to the pipe section.

In the class, the pipe section would be put under 60 or 70 pounds of water pressure with entrapped air at the top serving to provide an extended force effect. Through actual demonstration then, the pipefitters and machinists were taught how to open the flange in such a way that even though the line was under pressure, the opening should be accomplished without any liquid spraying on the men doing the work. Following the prescribed work procedures, the men would open the bolts on the side of the flange away from them, working around to their side and leaving the necessary bolts tight adjacent to them. When they would open on the far side, the water would spray out with considerable force, very vividly demonstrating the value of utilizing the proper techniques. During this class, which lasted about one hour, other points, such as the need for wearing protective equipment and safe techniques in the use of tools, were brought out where possible.

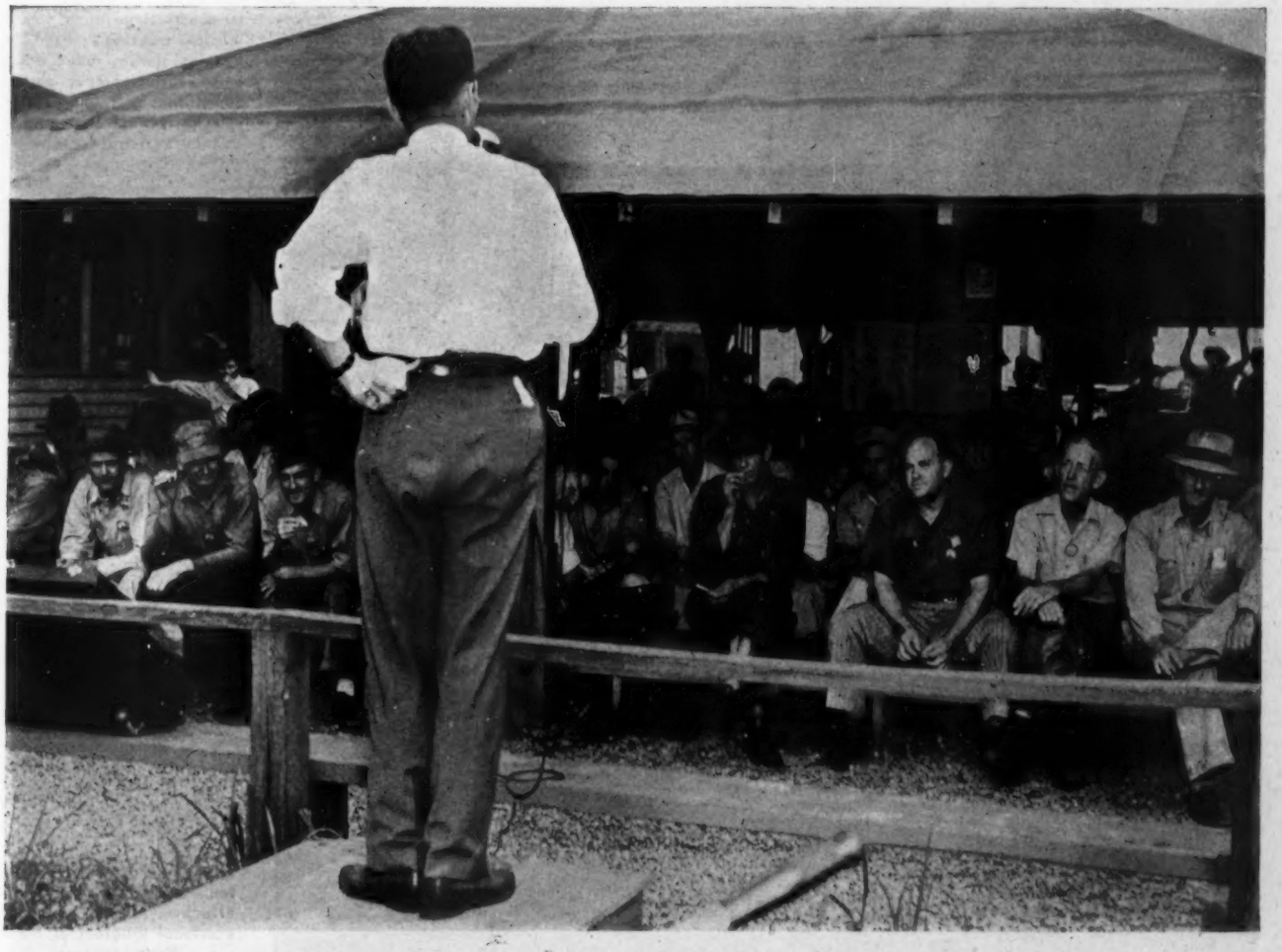
For an instructor for the class, it was decided that it would be most effective to have a man from the particular craft serve in that capacity. After considerable review, therefore, the instructor was selected from the craftsmen and experience has proven that this was a wise move. The manner of delivery of these instructors and the items of actual experience that they could inject into the discussion prove very interesting and effective.

Material Handling

A subsequent safety educational class was arranged on the subject of safety in handling materials. This class was designed for presentation to the members of all crafts. The subject matter consisted of showing of the National Safety Council slide sound film strip entitled "Safe Handling of Material," following which, actual demonstrations were held on proper techniques of lifting and the many other aspects of safety in handling materials. In these demonstrations, the instructor called on the men in attendance to take part in the particular activity being demonstrated. The intention was that every man be made to actually perform the task that was under discussion.

Other such classes are being planned and it is contemplated that these classes will be continued on a regular basis for some time. All indications are that the conducting of these classes has been one of the most effective means for teaching safety techniques and practices ever employed at Baton Rouge refinery.

Along with the requirements for added safety training, there was also, of course, a need for building up of safety spirit among the newer workers. For some years it had been the practice to hold "smoking-lot" safety meetings for the mechanical group. The smoking lots are located at a number of points throughout the refinery and furnish convenient places for holding safety meetings. It was accordingly decided to continue the plan of smoking-lot safety meetings to serve for building safety spirit; however, it was agreed that these meetings should be con-



Typical group gathered for a "smoking lot" safety meeting at Baton Rouge refinery

Demonstrating to a "smoking lot" meeting of need for keeping sleeves rolled down and wearing proper equipment for protection from splashes of corrosive chemicals.

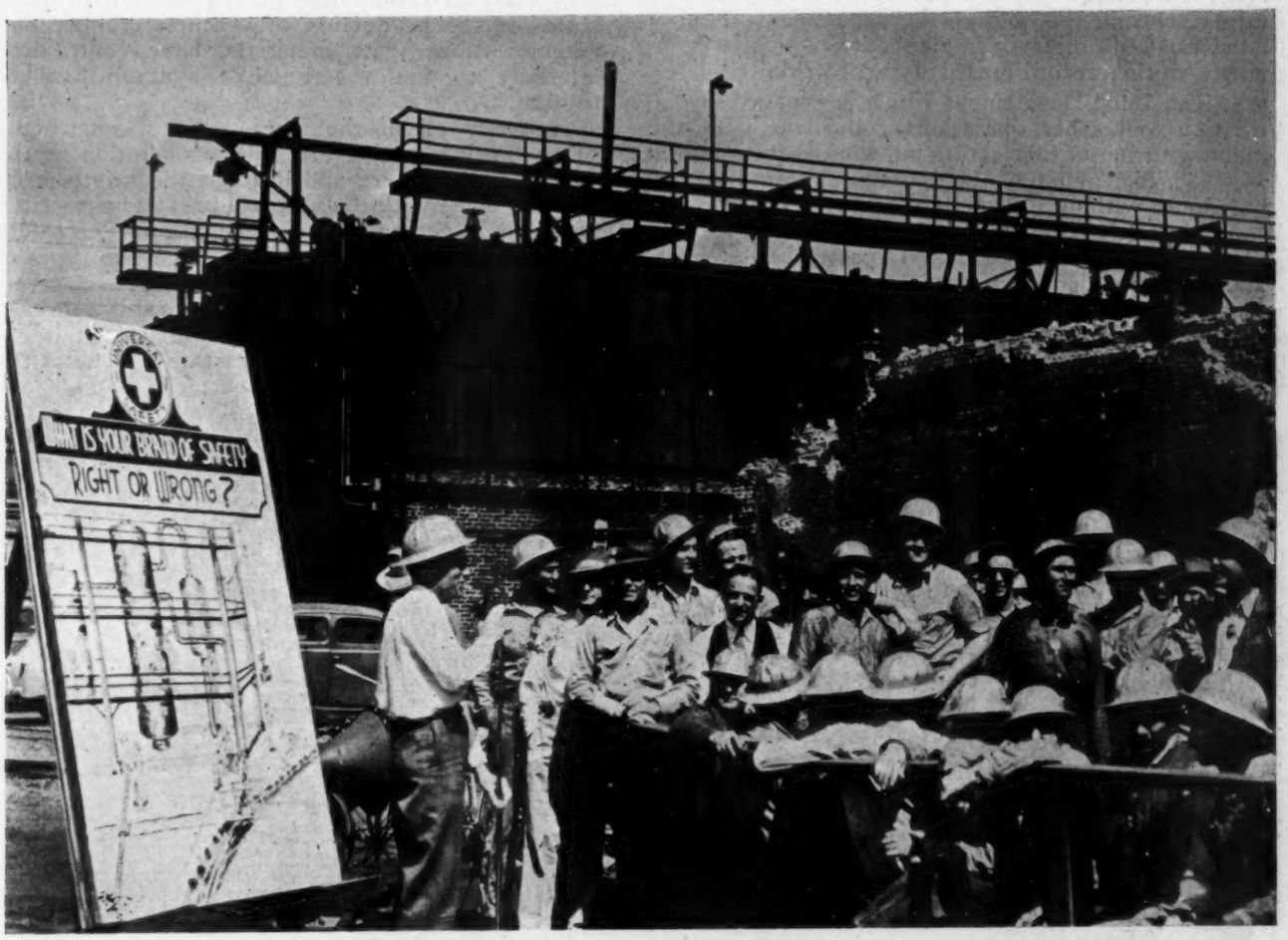
Close-up of a sample of the four- by six-foot signs used effectively in the safety educational program at Baton Rouge refinery.

ducted more frequently and on a broader scale. At the present time, therefore, the meetings are held at a rate of about four per year, and to adequately cover the entire refinery it is necessary to have a series of such meetings, one each day at about 15 smoking lots scattered over the entire refinery area. The meetings have been held immediately following the noon lunch period and usually last for about 20 minutes. Various subjects have been used for discussions at these meetings. In one interesting series of meetings, four-by-six-foot signs were made depicting the various types of injuries that contributed mostly to the accident experience for the previous year. The disabling injuries for the previous year were broken down into eight different types and one sign was made for each type, showing the number of injuries of that type illustrations on the signs. As many as 10 or 15 men from the audience had an opportunity to comment on the right and wrong aspects of the pictures.

Every effort is made to insure that the smoking-lot safety meetings are made relatively interesting and worthwhile. The Safety Department spends considerable time in preliminary arrangements, recognizing that the meetings have to be interesting in order to be effective. The results have been gratifying and plans are now being formulated for other novel meetings of this type.

Good Safety Record

It might be mentioned that Baton Rouge refinery is a pioneer in oil-refinery safety and has always maintained an outstanding safety record. The refinery



A microphone is being used here to encourage comments from the men considering a specific problem in safety.

experienced and with a drawing demonstrating the main feature required in the prevention of that type of accident. Two such sets of signs were made to enable complete coverage of the large smoking lots. A member of the Safety Department personnel served as commentator at the meeting. However, it was arranged to have several of the workmen speak on the prevention of those types of injuries that are most closely related with their particular crafts.

In another series of smoking-lot meetings, similar sets of signs were made up, on which were depicted various activities of the mechanical crafts done in the right and wrong way from a safety standpoint. A portable microphone was employed to permit obtaining comments from the audience on the various

has participated in the safety contest conducted by the National Safety Council for a number of years. Baton Rouge won first place for three straight years, the contests that ended in 1939, in 1940 and 1941. This record of three consecutive wins in the yearly contests has not been equalled by any other refinery. The refinery was third in the contests that ended in 1942 and 1943 and second in 1944.

These splendid safety records compiled at the refinery in recent years were attained through the cooperation of all the workers. In 1940 all workers of the refinery worked a period of 203 days without incurring a disabling injury. During this time, 4,216,000 manhours were worked, which was a world's record at the time for the petroleum-refining industry.

A number of departments have also established safety records which are outstanding:

1. The Refinery Process Division, which includes all of the refinery process operations, worked during the period from April 31, 1938, to August 3, 1940, accumulating 6,269,253 manhours, without a disabling injury.

2. The Mechanical Division which includes all departments engaged in mechanical work has a record which is also enviable. This division worked from December 9, 1939, to July 14, 1941, compiling 5,593,800 manhours without a disabling injury.

3. The Boilermaker Department, including all the welders, burners, and riggers, as well as the craftsmen usually designated as boilermakers, worked from August 17, 1938, to April 25, 1945, without a disabling injury. During this period, the department accumulated 3,316,533 injury-free manhours, which is probably a world's record for this type of work.

4. The Lube Department which is engaged in distillation and other operations coincident with the manufacturing of lubricating oil, worked from March 14, 1938, to August 17, 1944, accumulating 3,412,900 manhours without a disabling injury.

5. At the present time, the Refinery Police Department and the Storehouse Department have outstanding records which are continuing. The Police Department has worked about 1,900,000 manhours without a disabling injury, while the Storehouse Department has approximately 1,100,000 to its credit.

It may be of interest to know that Baton Rouge refinery is and has been for some time one of the largest oil refineries in the nation. The refinery produced better than 1,000,000,000 gallons of aviation gasoline during the war period and also still is one of the principal producers in the nation of synthetic rubber and synthetic raw materials.

Some of the first commercial plants for the production of synthetic rubber were constructed at Baton Rouge refinery. In fact former Rubber Director William Jeffers some time ago referred to Baton Rouge as "the cradle of the synthetic rubber industry." One of the first commercial-scale plants for producing Buna-type synthetic rubber from petroleum was completed at the refinery in 1941 and the first commercial-scale plant for producing Butyl-type synthetic rubber was placed in operation at the refinery early in 1943. These plants, along with other plants for the production of synthetic rubber and synthetic rubber raw materials, have contributed materially to the government's synthetic rubber program.

Practically all of the new facilities constructed during the war period are still in operation at the Baton Rouge refinery and likewise the safety problems that came with the new facilities and associated expansion in personnel are still present. The safety program in effect, centered around the two types of safety promotional meetings outlined above, seems to be having the necessary effect towards reducing accidents to the point, where before long it is expected that the refinery accident rate will be at the splendid low level of prewar years.

The sign is used to advantage in impressing the points discussed and also in getting comments from the group.

Rapid Analysis of Fischer Synthesis Catalyst

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ABSTRACT

Rapid methods for the determination of cobalt and thorium in Fischer catalysts are described. While the procedures were chosen for the speed with which the results can be obtained, the accuracy is found to be equally satisfactory. Cobalt is determined by titrating with ferricyanide to a "dead-stop" endpoint. Thorium is precipitated as the iodate and determined volumetrically. Details of the procedures as well as experimental results of analyses of both synthetic and actual samples are given.

The author is doing graduate work at Purdue University while on temporary leave from Standard Oil Company of New Jersey.

THE increasing interest of the petroleum industry in the synthesis of hydrocarbons from mixtures of hydrogen and carbon monoxide has created a need for rapid methods for the analysis of the catalysts employed. One of the most common catalysts used in hydrocarbon synthesis is the cobalt-thoria-kieselguhr mixture originated by Fischer. The properties of the catalyst are dependent upon the ratios of the three principal constituents, and, therefore, rapid methods for the accurate determination of these ratios are very desirable. The analysis is most conveniently carried out by determining the two most important components, cobalt and thorium, and calculating the kieselguhr base by difference. The purpose of this paper is to describe the methods that have been found most rapid and accurate in this laboratory for these analyses.

Determination of Cobalt

A variety of methods are available for the determination of cobalt. Of the many gravimetric procedures that have been proposed, the most common involve the precipitation of the cobalt with potassium nitrite or alpha-nitroso-beta naphthol. These methods are not only very time-consuming, but also are subject to interference by the iron and nickel usually present to some extent in Fischer catalysts.

One of the most accurate methods for the determination of cobalt is by electro-deposition. In this procedure the cobalt is deposited on a platinum electrode by the passage of an electric current through an ammoniacal solution. However, this method has the disadvantage of being rather lengthy and, furthermore, nickel is also deposited on the electrode.

Numerous volumetric methods have been proposed for the determination of cobalt. They are usually based on the formation of trivalent cobalt and subsequent titration with a reducing agent such as ferrous iron or iodide. None of these methods yields consistent results, because of the necessity of removing the excess oxidizing agent, the instability of the cobaltic ion in acid solution, and the slowness with which cobaltic hydroxide dissolves in reducing agents.

The method that has been found most satsfactory in this laboratory is a modification of the one described by Dickens and Maassen,[2] and Tomicek and Freiberger.[4] The method involves the titration of the cobalt with potassium ferricyanide in an ammoniacal solution, based on the reaction:

$$CoCl_3(\text{ammoniacal solution}) + K_3Fe(CN)_6 + NH_4OH \rightarrow CoCl_2OH(\text{ammoniacal solution}) + K_2NH_4Fe(CN)_6$$

Detection of Endpoint

Because of the intense red color of the oxidized cobalt, the endpoint must be detected electrometrically. Tomicek and Freiberger employed a pH meter for this purpose. It has been found that a simpler and equally accurate means of detecting the endpoint makes use of the "dead-stop" apparatus described by Foulk and Bawden.[3]

The dead-stop endpoint apparatus is shown schematically in Figure 1. It is quickly and easily assembled, and the only expensive item required is a fairly sensitive galvanometer. A very satisfactory one can be purchased for less than $50. The apparatus consists of two platinum-wire electrodes, a 1.5-volt dry cell, two carbon resistors, and a galvanometer.

The platinum electrodes must be prepared, since the ones obtainable commercially are generally not satisfactory for this purpose. Solder a copper lead wire to a 2-inch piece of 26-gauge platinum wire. Place the wire inside a 10-inch length of 5-mm. soft glass tubing so that the tip of the platinum barely sticks out the end of the glass tube. Seal the glass around the platinum, taking care not to melt the solder, and anneal carefully. Two electrodes prepared in this manner should not give a deflection when immersed in a solution of hydrochloric acid and connected through the galvanometer. If a deflection is observed under these conditions, the electrodes are either dirty or have been improperly prepared.

The dead-stop technique gives a very sharp endpoint in the titration of cobalt with potassium ferricyanide. When the titration is begun, the electrodes are immersed in the solution and connected to the galvanometer and polarizing unit. Although a potential of 10-20 millivolts is applied between the elec-

trodes, no current flows, because both the anode and the cathode are polarized, and the galvanometer pointer remains at zero. As the titration proceeds, the anode becomes depolarized by the ferrocyanide ions formed by the reaction. However, no current flows, since the cathode remains polarized. At the endpoint a very slight excess of ferricyanide ions is sufficient to depolarize the cathode. Both electrodes

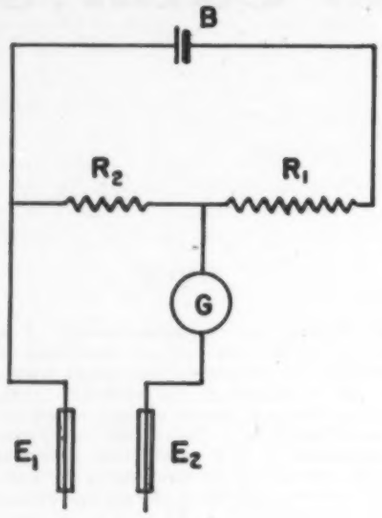

FIGURE 1

Dead-Stop Endpoint Apparatus

B — 1.5 volt dry cell

E_1 and E_2 — Two platinum wire electrodes

G — Galvanometer, Leeds and Northrup, Lamp and Scale Type. Sensitivity of 0.02 Microamperes per scale division

R_1 and R_2 — Two fixed resistors of such values that the potential between E_1 and E_2 is 10-20 millivolts (e.g., $R_1 = 1000$ ohms; $R_2 = 10$ ohms).

now being depolarized, current flows through the circuit and the galvanometer pointer is completely deflected.

Apparatus and Reagents

(1) Dead-stop endpoint apparatus, shown in Figure 1.

(2) Mechanical stirrer.

(3) Electrolysis beakers, 250 ml. tall form.

(4) Burette, 50 ml.

(5) Standard potassium ferricyanide solution, 0.05 N. Dissolve 62 grams of the salt in 1 gallon of water.

(6) Standard cobalt solution, 0.05 N. Dissolve 19.76 g. of cobaltous ammonium sulfate, hexahydrate in 1 liter of water.

(7) Sodium tartrate, 25 percent solution. Dissolve 125 grams of the dihydrate salt in 375 ml. of water.

Standardization of Reagent

Pipette 25 ml. of the standard cobalt solution into a 250-ml., tall form electrolysis beaker and add 2-3 ml. of HCl, 10 ml. of 25 percent sodium tartrate solution, and several pieces of clean ice. Remove all dissolved oxygen by dropping a piece of dry ice into the beaker. The vaporization of the CO_2 sweeps out the oxygen in about two minutes. If dry ice is not available, a nitrogen or natural gas scrubber will serve equally well. If the oxygen is not removed, it oxidizes part of the cobalt when the solution is made alkaline.

After the oxygen is removed, make the solution alkaline with ammonia and add 10-20 ml. excess. It is usually necessary to add more ice at this point to absorb the heat liberated by the neutralization of the acid with ammonia. The temperature of the solution must be maintained below 20° C. during the titration or the values obtained will be low. Place the beaker on the titration stand with the stirrer and electrodes well below the surface of the solution. Start the stirrer at a rapid rate to insure thorough mixing. Add the ferricyanide solution from a 50-ml. burette. As the endpoint is approached, momentary deflections of the galvanometer are observed, but the pointer quickly returns to zero position until the endpoint is reached. At the endpoint, one drop of the ferricyanide solution is sufficient to cause a permanent deflection of the galvanometer pointer to at least 20 scale divisions from zero.

The precision that can be obtained in the standardization of the ferricyanide against the cobalt solution is shown in Table 1. The potassium ferricyanide solution is very stable, and its strength changes only very slightly after standing for months. Normalities of several solutions that were used in the laboratory over a period of months are listed in Table 2. The solution darkens on standing, and a precipitate often slowly settles to the bottom of the bottle, but it has little effect on the normality of the solution.

The ferricyanide solution may be prepared as a primary standard if desired. This is shown in Table 1 where the theoretical normalities are compared with those obtained by titration of standard cobalt solution. For routine work, however, it was found more convenient to prepare the solution in gallon quantities and standardize it occasionally against a cobalt solution.

Analysis of Catalysts

Weigh 0.2-1.0 g. of the finely ground material into a 250-ml., tall form electrolysis beaker and add 20 ml. of aqua regia (3 parts HCl to 1 part HNO_3). If the catalyst contains carbon or organic material, ignite for 30 minutes at 1800° F. before transferring it to the beaker. Evaporate the acid almost to dryness on the hot plate; add another 20-ml. portion of aqua regia and evaporate to about 5 ml. The silica or clay base will not dissolve, but the two treatments with acid are sufficient to extract all the cobalt. It is unnecessary to filter out the undissolved silica, since its presence does not affect the titration.

Add about 20 ml. of water and 10 ml. of sodium tartrate solution, and cool in an ice bath. Add ice and

TABLE 1

Standardization of Potassium Ferricyanide Against a Cobalt Solution

$K_3Fe(CN)_6$ Solution	Titration	Normality of $K_3Fe(CN)_6$ Found	Normality of $K_3Fe(CN)_6$ Calculated
1	1	0.0691	0.0693
	2	0.0693	
	3	0.0689	
	4	0.0691	
2	1	0.1299	0.1299
	2	0.1300	
	3	0.1298	

TABLE 2

Stability of Ferricyanide Solutions

Age of Solution	NORMALITY Solution 1	Solution 2	Solution 3	Solution 4
One week	0.0639	0.0693	0.1226	0.1299
Three weeks	0.0637	.....	.....	.....
One month	0.0637	.....	0.1230	.....
Three months	.....	0.0683	0.1220	0.1296

TABLE 3
Interference Studies

Ion Added	Cobalt Added, Grams	Cobalt Found, Grams	Error, Milligrams
Al^{+++}	0.0299	0.0311	+0.2
Al^{+++}	0.1545	0.1549	+0.4
Sb^{+++}	0.1532	0.1526	−0.6
As^{+++}	0.1532	0.1534	+0.2
$B_4O_7^{--}$	0.1532	0.1535	+0.3
Cd^{++}	0.1534	0.1529	−0.5
Ca^{++}	0.1534	0.1527	−0.7
Cr^{+++}	0.1532	0.1535	+0.3
Cu^{++}	0.1532	0.1532	0.0
Fe^{+++}	0.0919	0.0918	−0.1
Fe^{+++}	0.1011	0.1016	+0.5
Li^{+}	0.1532	0.1535	+0.3
Mg^{++}	0.1534	0.1528	−0.6
Hg^{++}	0.1534	0.1530	−0.4
Mo^{6+}	0.1545	0.1548	+0.3
Ni^{++}	0.0506	0.0509	+0.3
Ni^{++}	0.1230	0.1227	+0.3
Ag^{+}	0.1534	0.1529	−0.5
Th^{++++}	0.0123	0.0127	+0.4
Th^{++++}	0.0308	0.0303	−0.5
Th^{++++}	0.1690	0.1683	−0.7
UO_2^{++}	0.1532	0.1531	−0.1
Zn^{++}	0.1534	0.1539	+0.5
Mn^{++}	0.1534	No endpoint—Mn^{++} interferes	
Fe^{++}	0.1534	Ppt. No endpoint Fe^{++} interferes	
V^{+++++}	0.1534	No endpoint V^{+++++} interferes	

solid CO_2, and proceed with the titration exactly as described under the standardization of the reagent.

Calculations

$$\%Co = \frac{\text{ml. } K_3Fe(CN)_6 \times \text{Normality} \times 0.05894 \times 100}{\text{Wt. of Sample}}$$

$$\%CoO = \frac{\text{ml. } K_3Fe(CN)_6 \times \text{Normality} \times 0.07494 \times 100}{\text{Wt. of Sample}}$$

Discussion

A study of the ions that interfere with the method was made, since Fischer catalysts usually contain significant amounts of other metals. The only elements that were found to interfere are manganese and vanadium. Vanadium would not interfere if tartrate were not added to the solution, since the vanadium is reduced by the tartrate and then reoxidized by the ferricyanide. The tartrate is added to prevent the hydrolysis of iron, aluminum, and thorium when the solution is made alkaline, and in the absence of these elements, its addition is unnecessary. The results of the interference studies are given in detail in Table 3.

A very high degree of precision and accuracy is obtained by the procedure. The accuracy is shown by the results in Table 4 and 5 of analyses of solutions containing known amounts of cobalt and synthetic samples prepared by adding known amounts of cobalt to various base materials. The precision that is found is illustrated by the results in Table 6 of a number of analyses of actual catalysts that were submitted to the analytical laboratory. Many of these analyses were made by non-technical analysts.

The length of time required for a titration is about five minutes. Consequently, a large number of samples can be analyzed in one day.

No correction for endpoint lag is necessary. In a blank titration of a solution containing potassium ferrocyanide, one drop of the ferricyanide causes a complete deflection of the galvanometer.

The usual method for the determination of thorium is based on its precipitation as the oxalate. The precipitated thorium oxalate is filtered, ignited to the oxide and weighed. This method is not very satisfactory for the analysis of cobalt-thoria catalysts, because the precipitate is often contaminated with the cobalt. In order for this method to be useful for the determination of thorium in the presence of excess cobalt, the thorium oxalate must be dissolved and reprecipitated. This makes the procedure very long and tedious and unsuitable for routine analyses. The fact that cobalt contaminates the thorium oxalate precipitate to a considerable extent is indicated by the results in Table 7 of analyses of two samples of Fischer catalyst, where the precipitate was washed, ignited, and weighed without a reprecipitation. The filtered thorium oxalate obtained in these analyses had a definite pink color from the cobalt.

Gravimetric methods based on the hydrolysis of thorium to $Th(OH)_4$ followed by ignition do not effect a separation from any iron and aluminum that might be present.

The method employed by this laboratory for the determination of thorium is a volumetric procedure based on the precipitation of $Th(IO_3)_4$ from a dilute nitric acid solution. The $Th(IO_3)_4$ is filtered, redissolved, and determined iodometrically. The following chemical reactions are involved in the method:

(1) $Th(NO_3)_4 + 4KIO_3 \rightarrow Th(IO_3)_4 + 4KNO_3$

(2) $Th(IO_3)_4 + 20KI + 12H_2SO_4 \rightarrow 12I_2 + Th(SO_4)_2 + 10K_2SO_4 + 12H_2O$

(3) $12I_2 + 24\,Na_2S_2O_3 \rightarrow 24\,NaI + 12\,Na_2S_4O_6$

The precipitation of thorium iodate from a nitric acid solution was the basis of a gravimetric method described by Chernikhov and Uspenskaya.[1] These authors stated that the precipitate had the formula $Th(IO_3)_4 \cdot KIO_3 \cdot 18H_2O$. Spectrographic analyses of the precipitate obtained in the method described below showed no trace of potassium. Analyses of the precipitate by this laboratory indicate that its formula is $Th(IO_3)_4 \cdot 4H_2O$.

Reagents

(1) Standard sodium thiosulfate solution, 0.1 N.
(2) Potassium iodide, 40 percent.
(3) Potassium iodate, saturated solution.
(4) Potassium iodate, 0.1 percent solution.
(5) Sulfuric acid, 10 percent.
(6) Starch solution indicator.

Procedure

Weigh a 1-gram sample of the finely ground cata-

TABLE 4
Titration of Known Cobalt Solutions

Titration	Cobalt Added, Milligrams	Cobalt Found, Milligrams	Error, Milligrams
1	12.3	12.7	+0.4
2	30.8	31.1	+0.3
3	30.8	30.3	−0.5
4	61.5	61.7	+0.2
5	92.5	92.4	−0.1
6	123.0	122.7	−0.3
7	153.4	153.6	+0.2
8	153.4	153.5	+0.1
9	153.8	153.9	+0.1
10	246.0	245.4	−0.6

TABLE 5
Analysis of Synthetic Samples

Sample	Percent Cobalt Added	Percent Cobalt Found
1	1.23	1.27
2	5.06	5.09
3	13.89	13.84
4	16.77	16.72
5	20.72	20.63

lyst into a 250-ml. beaker and add 20 ml. of aqua regia. Evaporate almost to dryness, add 10 ml. of nitric acid and evaporate to 3 ml. Dilute with water and filter into a 400-ml. beaker. Adjust the volume to about 300 ml.

Heat the thorium solution almost to boiling and add slowly with stirring 50 ml. of saturated potassium iodate solution. Digest on a hot plate until the supernatant liquid is clear; remove from the hot plate and cool in an ice bath.

Filter the cold solution through a Whatman No. 52 or 42 paper, and wash the precipitate thoroughly with 0.1 percent potassium iodate. Allow the last drop of the wash solution to drain out of the filter.

Dissolve the thorium iodate precipitate by directing a stream of hot 10 percent sulfuric acid onto the filter, collecting the filtrate in the original beaker in which the precipitation was carried out. When most of the thorium iodate is dissolved, force a hole in the bottom of the filter with the stirring rod and wash the remainder into the beaker with a stream of hot water from a wash bottle. Make certain that the last traces of precipitate are washed into the beaker. Heat the solution to boiling to dissolve any particles of thorium iodate that remain.

Cool the dissolved thorium iodate in an ice bath and add 5 ml. of 40 percent potassium iodide. Titrate the liberated iodine with a standard 0.1 N. solution of sodium thiosulfate, using starch indicator.

TABLE 6
Analysis of Various Catalysts

Sample	Percent Cobalt Found
1	22.00 22.02
2	25.02 25.00
3	18.90 19.04
4	26.33 26.11
5	26.49 26.60
6	7.18 7.26
7	29.53 29.61
8	50.50 50.20 50.30
9	27.40 27.40
10	1.77 1.75
11	5.09 4.99
12	11.88 12.06
13	51.40 51.52

TABLE 7
Variations in Thorium Analyses Precipitation of Thorium as Oxalate

Sample	Percent ThO_2
1	13.07 6.06
2	6.01 14.10

TABLE 8
Analysis of Known Thorium Solutions

Sample	ThO_2 Added	ThO_2 Found	Error
	Milligrams	Milligrams	Milligrams
1	26.1	26.2	+0.1
2	26.1	25.7	−0.4
3	26.6	26.8	+0.2
4	26.6	26.6	0.0
5	40.0	40.1	+0.1
6	40.0	39.8	−0.2

TABLE 9
Analysis of Fischer Catalysts

Sample	Percent ThO_2 Found
1	2.36 2.48
2	3.12 3.20
3	3.69 3.74
4	5.53 5.53
5	6.67 6.53

Calculations

$$\%\,Th = \frac{\text{ml. } Na_2S_2O_3 \times \text{Normality} \times 0.00967 \times 100}{\text{Wt. of Sample}}$$

$$\%\,ThO_2 = \frac{\text{ml. } Na_2S_2O_3 \times \text{Normality} \times 0.011 \times 100}{\text{Wt. of Sample}}$$

Discussion

A partial study of the interferences that would be encountered in the method by the presence of other ions was made. Ions, such as lead, that form an insoluble iodate interfere. The following ions were found to have no effect on the accuracy: Al^{+++}, Co^{++}, Cu^{++}, Mg^{++}, Fe^{+++}, and Ni^{++}.

The accuracy of the method for the determination of thorium was tested by analyzing a number of solutions of known composition, prepared from thorium nitrate tetrahydrate. The results of some of these analyses are listed in Table 8.

The precision of the method is shown by the results in Table 9 of analyses of typical catalysts that were submitted to the analytical laboratory.

A small blank is obtained, because of the thorium iodate wash solution retained on the filter. If the washing is thorough and the filter is allowed to drain completely, the thiosulfate titration is about 0.1 ml. For most accurate results the titration should be corrected for this blank, but since it is equivalent to only 0.1 mg. of thorium it can usually be neglected.

Summary

The methods that have been found most satisfactory for the determination of cobalt and thorium in Fischer synthesis catalyst are described.

The procedure for cobalt involves titration in an ammoniacal solution with potassium ferricyanide. The endpoint is detected by means of the dead-stop technique. The method is very rapid and accurate, and is not subject to interference by any of the other materials commonly associated with cobalt.

Thorium is precipitated as the iodate. The $Th(IO_3)_4$ is dissolved, reacted with iodide, and the liberated iodine titrated with thiosulfate. The method is more rapid and equally as accurate as the gravimetric method involving the precipitation of thorium oxalate.

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[3] Foulk, C. W., and Bawden, A. T., J. Amer. Chem. Soc., **48**, 2045 (1926).
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Physical Chemistry of Lubricating Oils

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THE multitude of engineering functions of lubricating oils and the growing severity of service conditions to which these materials are subjected (ranging to unprecedented pressures and temperatures in hydraulic servo-mechanisms, high-potential gradients in electric services, etc.) as well as the growing interest in the elucidation of their molecular structure, makes it appear desirable to assemble the often quite inaccessible scattered data of their physical properties and physico-chemical behavior. In this series of articles such data therefore will be presented, together with a framework of physico-chemical theory, in the absence of which the full theoretical and practical significance of experimental results could not be properly evaluated.

Following in general the now accepted sequence of topics in textbooks of physical chemistry, these articles are intended to appear in the following order:

I. P-v-t properties: density, thermal expansion, compressibility.

II. Surface tension, interfacial tension, emulsification.

III. Viscosity: Theoretical aspects, lubrication.

IV. Optical and Electrical Properties: Color (light absorption), refractivity and polarisation, dispersion, optical rotation, EI, conductivity, ions in oils, thermal properties.

V. Composition of Lubricating Oils. Distribution in molecular weight, bond-distribution.

VI. Phase Equilibria involving Lubricating Oils Solubility, Varporization, Adsorption.

VII. Reaction Kinetics.

I. P-V-T Data

BECAUSE of their low volatility, lubricating oils exist in the gaseous phase only at such low absolute (or partial) pressure that in this state they will always follow the ideal gas laws, nor can they ever reach the critical temperature without chemical decomposition. Only the liuid-state portion of the pressure-volume-temperature diagram of lubricating oils is therefore of any interest.

I. 1 Density

The density d, of liquids has long been found closely connected with their chemical composition. The quantity M/d, the Molecular Volume, can be fairly well calculated from bond increments which are found in most textbooks of physical chemistry. Close examination of the experimental molecular volume of various isomers of any one hydrocarbon, however, in comparison with the calculated volume will soon reveal deviations from the calculated average value, depending on the degree of branching, symmetry, etc. It has so far not been possible to predict the extent of these deviations[1] from "structural" increments. The reason for this is the often overlooked fact that the experimental molecular volume of liquids is really determined by two factors, the actual volume occupied by the molecules, and the so-called "free" volume. Variation of the latter, while sufficient to cause the deviations indicated above and also to materially affect other physical properties, are, however, quite small in comparison with variations caused by changes in composition, as is well illustrated in Table 1. It is for this reason that the C/H ratio in petroleum oils and quite a few related properties, such as heat of combustion, etc.[2,3,4,5] can be represented as density functions with an accuracy which is for engineering purposes sufficient, although not for any more thorough investigation of these properties. Figures 1a, and 1b provide evidence for the general trend of density vs. composition of pure hydrocarbons and lubricating oils. We see that density alone is, in the case of lubricating oils, a somewhat unreliable indicator of chemical composition. In combination with other data, however, the density is a valuable tool for the elucidation of the composition of lubricating oils, as will be shown in some of the following sections.

TABLE 1

The Molar Volume V, the Volume Occupied by Molecules V_b and the Free Volume V_f of some Liquid Hydrocarbons

HYDROCARBON	d_4^{20}	V	V_b*	V_f	V_f/V
n-Tridecane	.7567	243	190	53	.218
2, 10 Dimethyl Undecane	.7633	241	190	51	.211
n-Tridecene-1	.7658	237.5	184	53.5	.224
3 Methyl Dodecene-3	.7806	233	184	49	.210
2, 6 Dimethyl Undecadiene-1, 8	.7873	228.5	177	54.5	.224
2, 6 Dimethyl Undecatriene-1, 8, 10	.8005	222	170	52	.234
n-Tridecadiyne-1, 12	.8255	213	170	43	.202
1-Phenyl Heptane	.8590	205	156	49	.238
1-Phenyl-4, 4 Dimethyl Pentane	.9443	186.5	156	30.5	.164
1-Heptyl Cyclohexane	.8124	224	178	46	.205
Cyclotridecane	.8608	211	164	47	.222
				Average	.219

Density data from M. P. Doss, Physical Constants of the Principal Hydrocarbons.
* Calculated from Atomic Radii (based on covalent bond distances).

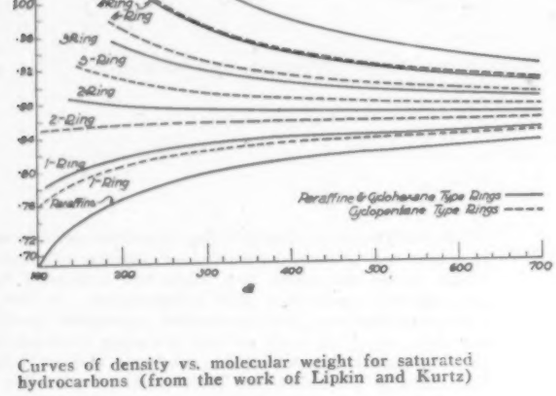
I. 2 The Coefficient of Expansion and the Temperature Coefficient of Density.

The expansion coefficient of liquids as defined by $\alpha = \frac{1}{V}\left(\frac{\delta V}{\delta T}\right)_P$ is temperature dependent, its temperature coefficient being given by $\frac{1}{V}\left(\frac{\delta^2 V}{\delta T^2}\right)$. The tem-

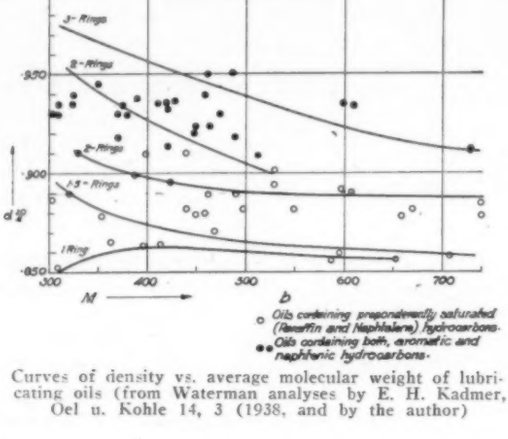
perature dependence of density is usually presented by the equation.[6]

$$d^t_y = d^{20}_y + a\ (t-20) + b(t-20)^2 \qquad (1)$$

The coefficient *a* often is mistakenly called expansion coefficient. Actually $a = \alpha \cdot d$. The physical meaning of these coefficients will be discussed in the next paragraph. We shall here concentrate on the relation between chemical composition and the coefficient *a*, which



Curves of density vs. molecular weight for saturated hydrocarbons (from the work of Lipkin and Kurtz)



Curves of density vs. average molecular weight of lubricating oils (from Waterman analyses by E. H. Kadmer, Oel u. Kohle 14, 3 (1938, and by the author)

FIGURE 1

Relation between density and chemical composition of hydrocarbons and lubricating oils

the type of hydrocarbon present. Table 2 and Figure 2 (from the work of Lipkin and Kurtz)[8] present these "universal" hydrocarbon density-temperature coefficients. The same investigators showed in a later communication[10] that each group of hydrocarbons—paraffins, naphthenes, and aromatics—give a distinct curve in the *a* versus *d* plot, reproduced in Figure 3. The naphthene-ring analysis of *aromatic-free* lubricating oils, which these authors proposed on the basis of the relationship

is indeed noteworthy[7] and of much value to the analysis of lubricating oils. Until very recently, it was generally held, that for all petroleum fractions *a* is solely a function of the density of the fraction under consideration. The "Gravity Tables" of the U. S. Bureau of Standards[9], are in fact, based on this assumption. Due to

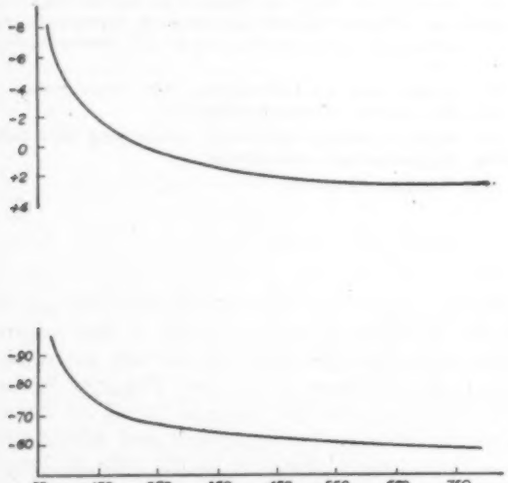


FIGURE 2

Temperature-density coefficients vs. molecular weight for hydrocarbons. (From the work of Lipkin and Kurtz)

the comparatively small deviations in composition from the average of most commercial petroleum products this erroneous assumption has so far not led to serious repercussions. Actually the coefficients *a* and *b* are simple functions of the molecular weight, and *not* of the density of the substance analysed, regardless of pictured in Figure 3 has so far proven the most reliable of all methods investigated.[11] Weight percent of naphthenic rings are thus calculated by:

$$\text{Wt.\% Naphthene Rings} = \frac{a_{unknown} - a_{paraffin}}{a_{naphthene} - a_{paraffin}} \times 100^* \qquad (2)$$

The solidification of crystallizing hydrocarbons is accompanied by contraction. The difference in volume between their solid and liquid state can as a good approximation be identified with their "free volume" in the liquid state. Glassy solidification of hydrocarbons (or any other organic substance) of less than 1000 molecular weight has so far not been observed to be accompanied by discontinuities in the volume-temperature curve. Lubricating oils which solidify without "clouding" are also free from any hump in their expansion-coefficient vs. temperature curve down to lowest temperatures, making it possible to apply the usual density-temperature correction factors over the entire temperature range. Not so with paraffin waxes and "wax"-bearing lubricating oils. The solidification of these materials is accompanied by considerable contraction at

TABLE 2

Dependence of the Temperature-Coefficients of Density on Molecular Weight 8

Molecular Weight	a x 10^5	b x 10^7
72	−97.5	−8.1
100	−86.8	−5.0
128	−80.5	−3.2
156	−76.3	−2.0
184	−73.2	−1.1
240	−69.5	±0
282	−67.6	+0.6
353	−65.0	+1.3
423	−63.4	+1.8
493	−62.1	+2.1
563	−61.3	+2.3
633	−60.6	+2.5
703	−60.1	+2.7
844	−59.3	+2.9

* Above $d > 0.840$ the denominator is taken as 26×10^{-5} gm $cm^{-3} \cdot C^{-1}$.

the melting temperature of the "wax" and over a somewhat wider temperature range beginning with the cloud point of the oil. Table 3 and Figure 4 provide the few numerical data thus far available. The difference between the pure compounds and commercial paraffin waxes should be noted, since the diminishing of $\Delta^{s}_{L}d$ with decreasing degree of purity is a generally observed phenomenon, and is apparently due to incomplete crystallization. The free volume can therefore only in pure substances be related to $\Delta^{s}_{L}d$.

I. 3 Compressibility

The compressibility, defined by $\beta = \frac{1}{V}\left(\frac{\delta V}{\delta P}\right)_T$ has for technical reasons only recently[12,13,14] been more thoroughly investigated. The rapid development of oil-filled high-pressure hydraulic systems and similar engineering applications just now began to stimulate other than theoretical interest in the compressibility data of

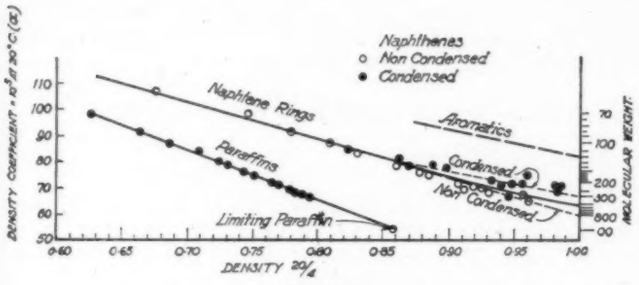


FIGURE 3

Curves of density-temperature coefficient vs. density of hydrocarbon. (From the work of Lipkin and Kurtz)

lubricating oils. All of these so far available data, according to Dow and Fink,[14] can be represented with good accuracy by the simple equation:

$$[d_P = d_0(1 + mp - np^2)]_t \qquad (3)$$

where d_P = density at pressure p_1 d_0 = density at atmospheric pressure, at the same temperature t. Some numerical values of m and n are tabulated in Table 4. Compressibility data of hydrocarbons and lubricating oils are collected in Table 5.

The rapid decrease of β with increasing pressure is readily understood if we remember that intermolecular repulsive forces which have to be overcome when compressing a liquid increase with the inverse fourth power of the volume. Just as many other liquids,[12] oils solidify at elevated temperatures if only sufficient pressure *is brought* to bear.[15,16,17] In two points do lubricating oils differ markedly from pure compounds: They do not show the characteristic contraction in the course of this solidification (which can be observed viscosimetrically only). The transition from the liquid to the solid state and vice versa is quite slow, the "solid" (or better "paste") persisting for a short while even after release of pressure. The pressure at which these transitions of oils take place range between 3000 and 5000 Kg cm^{-2}, which is of the order of the pressure at which attractive and replusive forces in these oils just balance. From thermodynamics we know that the change of internal energy of a fluid with pressure is given by:

$$\left(\frac{\delta E}{\delta P}\right)_T = T\left(\frac{\delta V}{\delta T}\right)_P - P\left(\frac{\delta V}{\delta P}\right)_T \qquad (4)$$

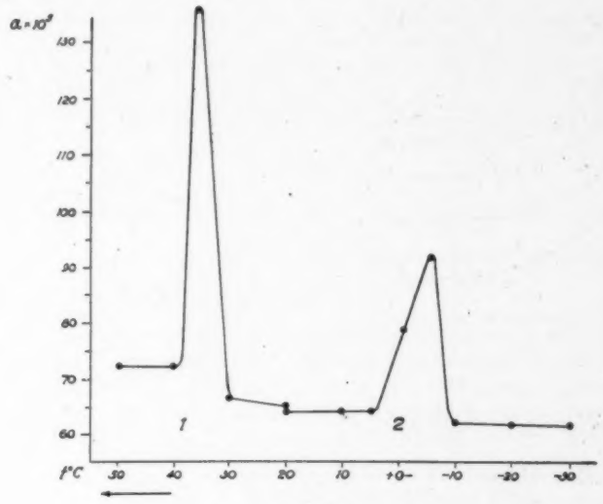
where the first term on the right is expressive of the attractive forces within the fluid and the second of the repulsive forces. It is evident that at a certain pressure the two terms will become equal, making $(\delta E/\delta P)_T = 0$. This pressure is given by: $P'_i = T\left(\frac{\delta P}{\delta T}\right)_V = T\alpha/\beta$, (5)

TABLE 3

Solidification Point Contraction of Pure Hydrocarbons and Some Petroleum Fractions

SUBSTANCE	m.p. °C.	Contraction (Percent of Liq. Val.)	Reference
N-Tetracosane	50.6	19.8	a
N-Dotriacontane	69	16.9	a
Paraffin Wax D	72	11.8	b
Paraffin Wax A	52	11.2	b
Microcristalline Wax A	71	7.1	b
Penna 150 Neutral	(—5)	1.2	

a W. F. Seyer and E. Yatabe, ACS Meeting Sept. 1937, p. 25 Petroleum Div.
b A. Kinsel and J. Phillips, Ind. Eng. Chem. Anal. Ed., 17, 152 (1945).



1. Pennsylvania 150 neutral, containing 20 percent paraffin wax 50/52.
2. Pennsylvania 150 neutral.

FIGURE 4

Variation of expansion coefficient of wax-bearing lubricating oil with temperature.

the pressure increase per degree temperature at constant volume. Since β decreases faster with increasing pressure than α, $\left(\frac{\delta P}{\delta T}\right)_V$ increases somewhat with pressure. This factor $(\delta P/\delta T)_V$ is not only of some practical interest (giving us an idea of the pressure increase when heating an oil-filled vessel without expansion provisions) but also theoretically important, since the ability to predict its numerical value is one of the best checks of the usefulness of a theory of the liquid state. A few such values have been calculated from available expansion and compressibility data and assembled in Table 5.

As to be expected, adiabatic compression of liquids is accompanied by a noticeable temperature rise. For most organic liquids and also lubricating oils, this rise amounts to about 10° C. for the first 1000 Kg cm^2, which is certainly less than for gases and for engineering purposes nearly inconsequential, but sufficient to

TABLE 4

Values of the Density-Pressure Coefficients m and n (From the work of R. B. Dow and C. E. Fink 14)

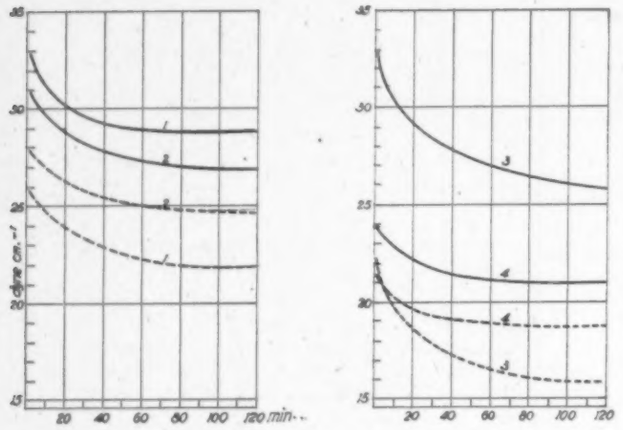
Temp. °F.	m[(psi)$^{-1}$]	n[(psi)$^{-2}$]
30	4.02 x 10^{-6}	7.0 x 10^{-11}
60	4.19	6.4
100	4.38	5.7
140	4.53	5.1
180	4.63	4.7
220	4.68	4.4

TABLE 5

Values of Compressibility β, $(\delta p/\delta T)v$, and Internal Pressure Pi, of Some Hydrocarbons and Lube Oils

Substance	Vis @ 20° C Poise	t °C.	p kg/cm²	β kg⁻¹cm²	$(\delta p/\delta T)v$ kgcm⁻²°K⁻¹	Pi kgcm⁻²	Ref.
N-Pentane....	.0024	50	1—1000	13.3×10^{-5}	7.1	1800	a
N-Pentane....	....	50	3000—4000	3.2	15.1	1360	..
N-Decane.....	.008	50	1—1000	8.1	7.8	2020	a
N-Decane.....	....	50	3000—4000	2.1	20.0	1960	..
Lube oil, light.	.095	40	1—1000	4.9	11.0	2950	b
	@ 38° C.	40	1000—2000	3.2	13.0	2570	..
Lube oil, heavy	.70	40	1—1000	4.5	12.0	3250	b
	@ 38° C.	40	1000—2000	3.1	13.5	2750	..

a P. W. Bridgman 12. b R. B. Dow and M. R. Fenske 13.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min.
1) Solvent refined lube oil d_4^{20} = 0.896, η_{20} = 2.8 Stokes.
2) Conventional ref. lube oil d_4^{20} = 0.920, η_{20} = 4.2 Stokes.
3) Lube oil containing Polyisobutylene d_4^{20} = 0.899, η_{20} = 3.1 Stokes.
4) Synthetic (Fischer-Tropsch) lube oil d_4^{20} = 0.858, η_{20} = 3.5 Stokes.
(From the work of K. O. Müller, Oel u. Kohle, 14, 365 (1938))
new oil
oxidized oil

FIGURE 5

Change of surface tension of lubricating oils with time (Determined by du Nouy's method).

warrant attention in laboratory high-pressure investigation.

This also indicates that one has to differentiate between isothermal and adiabatic compressibility of liquids (just as of gases).[23] The factor "m" in equation (3) is—at low pressures—equal to the isothermal compressibility. The adiabatic compressibility is somewhat smaller than the isothermal and is most conveniently determined by calculation from the latter according to the rules

$$(\delta - 1) = \frac{T \cdot \alpha^2 \cdot u_s^2}{c_p \cdot J} \quad \text{or} \quad 1 - \frac{1}{\delta} = \frac{T\, v\, \alpha^2}{J\, c_p\, \beta}$$

where: δ = ratio of isothermal to adiabatic compressibility = c_p/c_v, c_p = spec. heat at const. pressure, J = mechanical heat equivalent T = absolute temperature, α = expansion coefficient, u_s = velocity of sound in the oil, v = specific volume, β = isothermal compressibility. In most lubricating oils δ ranges around 1.135 (1.12 for fatty oils).

The propagation velocity of sound in fluids u_s is connected with compressibility through the relation: $u_s = \sqrt{g \frac{dp}{d\rho}}$, where: ρ = the density of the fluid. From the data on Table 4, we obtain for typical lubricating oils a sound-velocity of 3500-4000 m/sec. From Bridgeman's rule: $u_s = v^{2/3}\kappa/2K$, where: v = volume per molecule, κ = heat conductivity, K = Boltzmann's constant, we obtain for a typical lubricating oil (V = 400) about 3500 m/sec in good agreement with the compressibility relation. The magnitude of u_s is quite remarkable—"simple" liquids ranging between 1200 and 2000 m/sec—but consistent with the respective compressibilities. These values of u_s should nevertheless be treated with caution until experimental data become available, since it is to be expected that high viscosity will not be without influence on u_s.

II. Surface Tension and Related Phenomena

II. 1 Surface Tension

The surface tension of a liquid is a measure of the force (per unit length) which tends to reduce its surface to the smallest possible value. In the case of pure liquids it is independent of the size of the surface. It has since the time of Laplace (1806) been recognized as a measure of the internal (cohesive) forces characteristic of the liquid state. In the previous section we have seen that the internal pressure varies very little for a wide range of lubricating oils, whence it is not surprising to find that the surface tension of lubricating oils varies also only within very narrow limits from oil to oil. Comparatively few measurements of this property have therefore been published. What there is provides, however, sufficient additional insight into the nature of the liquids under consideration to be well worth recording, especially after evaluting the derived function, the molar surface energy and the Eötvös-Constant. The molar free surface energy $\Delta F\omega$ is defined by $\Delta F\omega = \sigma V^{2/3}$, where σ = Surface tension, and V = Mol volume. The total molar surface energy is $\Delta E\omega = \left(\sigma - T\frac{d\sigma}{dT}\right) \cdot V^{2/3}$. Applying Van der Waals' familiar concept of corresponding states (according to which the "reduced" cohesive forces in all "normal" liquids are equal when measured at a temperature corresponding to the same value of the ratio (temperature of measurement/critical temperature = reduced temperature) to the surface energy, Eötvös

TABLE 6

Surface Tension σ, Molar Free Surface Energy $\Delta F\omega$, Total Surface Energy $\Delta E\omega$, and Eötvös Constant K_E of Lubricating Oils

SUBSTANCE	Ref.	M	t °C.	σ	$\Delta F\omega$	K_E obs.	K_E calc.	$\Delta E\omega$	$\frac{\Delta E\omega}{\Delta E_{vap}}$*
USP White Oil, light.....	a	290	20	30.05	1448	3.1	3.14	2658	.14
USP White Oil, heavy.....	a	449	20	31.67	2040	(3.16)	4.06	3490	.121
Cyclic Oil d=.966.....	a	365	50	32.47	1705	4.00	3.22	3075	.155
Diesel Lube, heavy.....	a	540	20	32.80	2350	4.34	4.11	4800	.140
Penn Bright Stock.....	a	790	50	30.30	2790	5.50	5.04	4850	....
Coastal Type Lube.....	b	410	20	32.74	1860	3.52	3.50	3080	.133
Penn Bright Stock.....	b	850	20	33.75	3250	5.61	5.28	5550	....

a This work. b Tanss and Dreifuss, Petroleum 24, 1383 (1928). * ΔE_{vap} Estimated with Cragoe's formula.

and Ramsay and Shields found, that all "normal" liquids follow the law:

$$\frac{d\Delta F\omega}{dT} = \frac{\Delta F\omega}{T_c - T - 6} = K_E \sim 2.12 \qquad (5)$$

K_E is even for "normal" liquids equal to 2.12 only below molecular weights of about 100, for higher molecular weight its value increases according to a rule formulated by Walden.[18]

$$K_E = 1.90 + 0.011 \Sigma n \sqrt{A} \qquad (6)$$

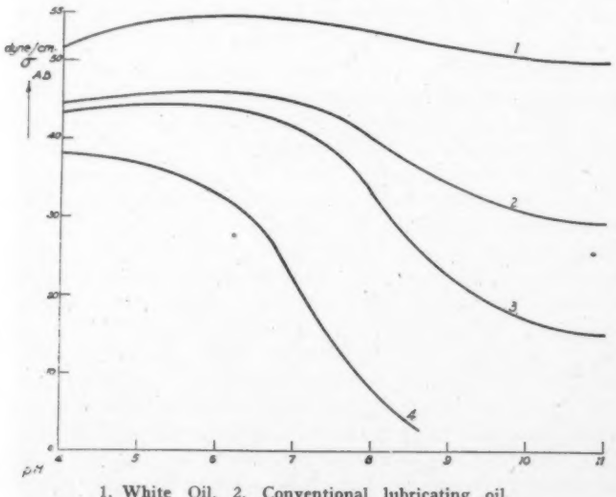
where n = number of atoms of each element in the molecule considered, and A = the atomic weight of same. Comparing K_E values thus calculated with the K_E of lubricating oils assembled in Table 6 we see that lubricating oils fall in the class of "normal" liquids, being not only non-associated but as can be judged from their usually comparatively higher K_E—rather below "par" in cohesion. The same can be followed from the $\Delta E\omega$ data. Van Urk[19] derived that for normal liquids $\frac{\Delta E\omega}{\Delta E_{vap}}$ (ΔE_{vap} = the energy of vaporization) should be about 0.28. Table 7 shows that for lubricating oils and similar hydrocarbons this ratio is much smaller than 0.28.

These phenomena are in part due to: a) the fact that it is probably not permissible to apply the rules of "corresponding" states to lubricating oils (or any substances within that molecular-weight range); b) the enriching of more surface active components of these oils in the surface. The latter statement is based on the following observations:

Some of the lubricating oils examined exhibit a slight curvature in their σ vs. T curve, or in other words the second derivative $d^2\sigma/dT^2 \neq O$. From equation (5) follows that

$$T\frac{d^2\sigma}{dT^2} = -\frac{dC_V}{d\omega} \qquad (7)$$

where C_V = the specific heat of the liquid, and ω = the size of its surface. This means that, whenever $d^2\sigma/dT^2 \neq O$ the specific heat of the surface differs from the specific heat within the bulk of the liquid indicating that either the composition or the molecular arrangement of the surface layer is different from within the bulk of the liquid. The few second derivative values of lubricating oils so far observed are quite small (of the order 2×10^{-4} to 5×10^{-3}) but in qualitative agreement with another observation, the time dependence of the surface tension of such oils, when examined with the du Nouy tensiometer,[20] as depicted on Figure 4. Such time dependence of σ always points toward changes in composition of the surface layer taking place during measurement. All surface-tension measurements reported above have for this reason been performed by static methods (e.g. capillary rise), dynamic methods giving unreproducible unreliable results with such lubricating oils.



1. White Oil. 2. Conventional lubricating oil. 3. Lube Distillate. 4. Oxydized white oil

FIGURE 6

Interfacial tension between oil and buffer solutions of various pH values.

A better explanation has been offered by Adam[20] who showed that interpretation of the surface tension as "surface pressure" F leads to

$$\frac{d}{dT}\left(\frac{F}{No}\right) = \frac{K_E}{nN^{2/3}} = 1.395 \times 10^{-16}\,\frac{K_E}{n}\,, \frac{d}{dT}$$

$$(FA) = R = 1.37 \times 10^{-16}$$

where: No = number of molecules per square centimeter of surface, n = number of molecules in the thickness of the surface layer, A = area per molecule. The Eötvös constants K_E becomes thereby a measure of the thickness of the surface layer: $K_E = 0.985n$. If the molecules in the surface layer are x times as long as thick then their number in the surface is $nx^{2/3}(N/V)^{2/3}$ and K_E increases in the ratio $x^{2/3}$. The measurements by Tausz, Freund and the author do indeed follow a proportionality $K_E \propto M^{2/3}$ quite well, indicating that those portions of a petroleum lubricating oil which are present in the surface layer follow a fairly regular structural pattern.

II. 2 Interfacial Tension

In the previous paragraph only the surface tension at the liquid-air (vapor) interface has been treated. A field of much interest, though yet less well understood is the "surface" tension at the interface of two liquids. The only secure theoretical background for the interpretation of interfacial tension σ_{AB} data are contained in the following two equations:

TABLE 7

Interfacial Tension σ_{AB} and Spreading Coefficient W_s of Lubricating Oils Against Water

OIL	t °C.	σ_A	σ_B	σ_{AB}	W_S	Ref.
USP—White Oil heavy	20	31.67	72.5	56	—15.1	a
300—Coastal Solvent Raffinate	20	32.1	72.5	45	— 4.4	a
Turbine Oil A	25	....	....	48.5	—	b
Same oxydized 150 hours	25	....	....	10.0	—	b
Oleic Acid (for comparison)	20	32.5	72.5	15.5	+24.5	c

a This work. b V. Fuchs, Wilson and Edlund, Ind. Eng. Chem. 33, (1941). c S. Glasstone, Textbook of Physical Chemistry, New York, 1943, p. 477.

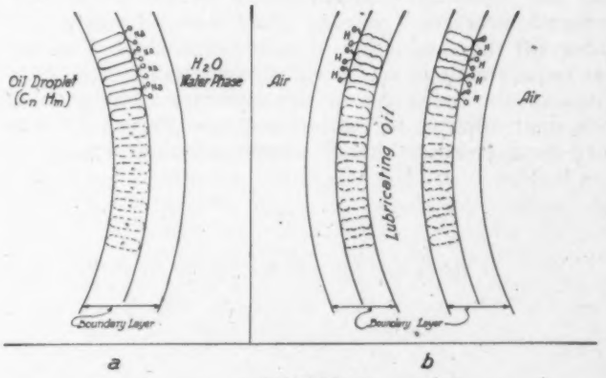


FIGURE 7

The molecular structure of adsorbed and oriented boundary layers: a—at the oil-water interface of a lube oil emulsion (Na-fatty acid soap as emulsifier); b—of the lamellae between foam bubbles or lube oil-air foam (an acid compound, e.g. oxidized oil, as form producer). Both demulsifiers and anti-foam agents act essentially by dissolution and/or disorientation of these boundary layers.

The net work done in spreading 1 cm² of liquid A over liquid B = $\sigma_A - \sigma_B + \sigma_{AB}$ and the adhesional work between A and B is

$$W_{AB} = \sigma_A + \sigma_B - \sigma_{AB} \qquad (8)$$

The liquid A will therefore spread over B only when $W_{AB} > 2\sigma_A$. W. D. Harkins[21] called ($W_{AB} - 2\sigma_A$)

the spreading coefficient W_s. This coefficient is positive —i.e. σ_{AB} is quite small—whenever there is close chemical affinity between A and B. A number of typical values of W_s have been assembled in Table 7. Since, as will be more thoroughly discussed in the following paragraph, the boundary tension of a mixture is determined by the component producing the smallest σ_{AB}, the coefficient W_s is extremely sensitive to the presence of small amounts of "active" non-hydrocarbon materials present in lubricating oils. These "active" compounds very often have acidic character, so that the effect will be accentuated by the use of alkaline water as substrate. For this reason Vellinger[22] suggested to use σ_{AB} vs. pH curves, such as illustrated in Figure 6, for the control of lubricating-oil refining processes. But the writer could not find this method to give any more information than the less well defined but more convenient demulsibility test. Oxidized lubricating oils show the expected decrease in interfacial tension against water[22,23] already in the early stages of aging. This decrease is, however, so much more rapid than the general deterioration of the oil that its determination alone could hardly serve to appraise the status of a used oil.

II. 3 Emulsification and Foaming

The last mentioned phenomena point toward the existance of a physical principle which had first been recognized by J. Willard Gibbs (1878): the enrichment of the component with the lowest boundary tension at the boundary, independent of the nature of the boundary, be it liquid-gas, liquid-liquid, or liquid-solid. Gibbs' law, governing these phenomena is best known in the form:

$$\Gamma_2 = -\frac{1}{RT}\frac{d\sigma}{d\ln a_2} \simeq -\frac{1}{RT}\frac{d\sigma}{d\ln c_2} \qquad (9)$$

where Γ_2 = the excess concentration of solute per unit area of surface, and a_2, c_2, = its activity and concentration, respectively.

This relation does well explain the mechanism of emulsification and foam formation, since the reduction of boundary tension is the first requisite of emulsification and foaming (emulsification of gas in liquid). Reduced interfacial tension alone does, however, not suffice for the production of stable emulsions. The second requirement is, as is well known today, the orientation of the molecules in the interface in accordance with their affinity for each phase (see Figure 7). The third requirement is that this boundary layer has a certain mechanical stability and electrical potential, preventing coalescence of like phases. The past two decades have seen rapid advance in our knowledge of the physics of surface films,[27] but complete quantitative treatment of emulsification is still lacking. Qualitatively the above mentioned mechanism has been of considerable help in the solution of two troublesome problems in lubrication: emulsification of oil and water and foaming. Theoretically both problems could be solved by freeing the lubricating oil from all non-hydrocarbons. Practically this is a valueless procedure. As soon as the oil comes into service it either forms (by oxydation) or otherwise incorporates surface-active components. The problem could therefore only be solved by synthesizing additives which will be most strongly adsorbed in the interface (even lowering interfacial tension) but due to their iso-diametric constitution will not take any preferred position (orientation) in the interface and/or (by plasticizing action) prevent the formation of stable surface films by other surface-active materials which happen to be present in the lubricating oil. The literature describing such de-foaming and demulsifying products adds to more than 300 titles, it is therefore clearly beyond the scope of this paper to enter into a more detailed discussion of such additives.

The adsorption at the liquid-solid interface will be treated in the section on phase equilibria.

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This is the first of an article in three parts—Parts 2 and 3 will appear in succeeding issues.

Sulphuric Acid Refining In the Production of Aviation and Motor Fuel

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THE outstanding features of recent motor-fuel technology have been the extensive use of catalytic-cracking processes in the petroleum industry and the ever-increasing utilization of coal and oil shale for the production of motor fuel. While catalytic cracking has chiefly been developed and applied within the American petroleum industry and by American petroleum companies operating outside the United States, the question of substitute fuel was taken under consideration relatively early in some of the European countries.

Preceding World War II sulphuric-acid refining, with its various techniques, constituted an integral part of the operations for finishing thermally-cracked petroleum fractions. There have been ample reports on research and refining operations in this field, which have been exhaustively surveyed in the literature.[1]

The object of the present paper is to indicate the role the latest developments in the techinque of motor and aviation fuel production have assigned to sulphuric-acid refining. Its position in regard to the catalytic cracking of petroleum fractions can be seen by reference to the technical press of the last few years. The data for motor and aviation fuel produced from other materials than petroleum are derived either from operations with a pilot plant, as described in an earlier issue of this journal,[2] or from actual refinery runs with an equipment of the same type as this pilot plant.

Sulphuric acid has two functions in connection with the catalytic cracking of petroleum fractions: the drastic removal of olefins for the preparation of aviation base stock and the light finishing treatment of either aviation base stock or motor gasoline. The first mentioned application is dealt with in an article on fluid catalytic cracking.[3] Hydrogenation and catalytic treatment are mentioned as alternative methods for eliminating olefinic compounds in order to improve antiknock qualities. Acid treatment is shown to be of considerable interest, owing to the possibility of using spent alkylation acid. Another paper on the same subject[4] mentions catalytic treatment (retreatment), polytreating with UOP catalyst and sulphuric-acid refining. Advantages of the acid treatment are stated to be simultaneous desulphurization in the case of stocks with a high sulphur content, and a considerable simplification of the equipment required. Improvement in quality is less marked with the acid treatment than with the two other methods. This can be offset, it is said, by operating the first stage cracking step at higher conversion levels.

Reference is also made to aviation blend stock, obtained by catalytic cracking and retreating, followed by a controlled temperature acid treatment.[5] It is reported that preliminary information indicated that high-temperature storage conditions in the tropics called for aviation gasoline with great stability.

As far as motor gasoline is concerned, the acid treatment aims chiefly at desulphurization.[6] In motor gasoline obtained by the fluid catalyst process with West Texas feed the sulphur content is above specification, but it can be improved by a light acid treatment.[7] A comparison of the relative merits of the sulphuric acid treatment and catalytic refining for the removal of sulphur shows that catalytic desulphurization is not often used for cracked stocks, because the thiophene type sulphur compounds seem to be unaffected by the process.[8] Sulphur reduction by catalysis has, however, been found to be very effective on straight-run stocks, if due consideration is given to the problem of combating corrosion, which is comparable in all respects to the corrosion in cracking operations.[9] As regards such sulphur compounds as occur in cracked distillates, however, experimental data show that, even when nickel catalysts—which have a marked affinity for sulphur—are employed, the sulphur reduction during the period of greatest catalytic activity is only nominal, and the thiophene compounds are apparently unaffected. Hydrogenation is recommended as an alternative to the sulphuric acid treatment of stocks with relatively high sulphur content.[10]

Gasoline Other Than Petroleum

Reverting to the acid refining of gasoline from other sources than petroleum hydrocarbons, typical examples will be given of results obtained by treating light spirits from the low-temperature carbonization of lignite as well as benzole and light shale-oil fractions. Progress in the refining technique of cracked petroleum distillates by the use of means for controlling contact time and treatment temperature[1] has been applied with success to this field. Older methods were chiefly confined to the use of diluted acid (about 80 percent) in order to prevent excessive losses of valuable hydrocarbons, formation of hard acid sludge, poor separation, corrosion of

the rerun equipment and other inconveniences. It had not been possible to take advantage of the considerably higher desulphurization efficiency of acid of higher concentration. Also the fact that, even allowing for the lower cost of the less concentrated acid, it is cheaper to use small amounts of strong sulphuric acid (95 percent), rather than large amounts of, say, 80 percent acid, had to be left out of account. Firstly by employing centrifugal separators, with or without cooling equipment, it has been possible to limit the action of the sulphuric acid chiefly to desulphurization and to keep undesired effects, within certain limits, under strictly scientific control.

Thus, on treatment with 9 percent by weight sulphuric acid (95 percent), in a gravity settling plant of the continuous countercurrent type, a lignite low-temperature distillate with the following properties:

Specific Gravity	0.814
I. B. P.	62° C
50 percent over at	200° C
F. B. P.	290° C
Sulphur	2.1 Percent

gave a gasoline fraction (195° C. F. B. P.) with 1.3 percent sulphur and 150 mg potential gums per 100 ml. Refining losses in this operation were 17 percent. The same raw product, treated in a plant with centrifugal separators, with a contact time of 1 minute per stage, but (during the test described) without cooling at any stage, with 5.8 percent acid (95 percent) gave a 195° C. endpoint distillate with 1.0 percent sulphur and 2 mg potential gums per 100 ml. The refining losses in this operation were 6.5 percent. When the sulphuric acid was increased by 9 percent by weight (viz. the same amount as used when operating with gravity settling), the losses rose to 12 percent. The sulphur content of the finished gasoline (195° C. F. B. P.) was only 0.43 percent, however, as compared to 1.3 percent gravity settling.

Another lignite low-temperature distillate with the following properties:

Specific Gravity	0.808
I. B. P.	53° C.
25 Percent over at	100° C.
F. B. P.	190° C.
Sulphur	2.4 Percent

presented a considerably more difficult problem in respect of desulphurization. Acid up to 19 percent (95 percent) has been tried in a settling plant, without reducing the sulphur content in the finished gasoline (170° C. cut) to below 1.2 percent. The acid was added in three consecutive operations, each supplying about one third of the total amount of acid used. A neutralization stage followed each acid treatment. Counter-current was not suitable owing to the consistency of the acid sludge. Refining losses were 30 percent.

In a two-stage countercurrent plant with centrifugals limiting the contact time in each stage to two minutes, it has been possible to obtain a finished gasoline (170° C. endpoint) with only 0.70 percent sulphur, water white and color and gum stable, when the distillate was passed three times through the plant, without any neutralization except after the third pass. Fourteen percent of 95 percent sulphuric acid was used, equally distributed for each pass. Refining losses were only 16 percent in this case. In both the settling and the centrifugal operations the raw stock was cooled previous to each acid treatment in order to keep the final temperature below 40° C. The concentration of the acid used was always 95 percent, as lower concentrations were ineffective as regards desulphurization.

Benzole refining up to the outbreak of the second war has been discussed in detail in the literature.[11] In this industry, too, technique of acid treatment has been improved, thanks to the progress achieved in the control of the treating factors. Concentrated sulphuric acid, with its inherent advantages, can be used without any of the troubles referred to earlier, if plants are equipped with mechanical means for instantaneous sludge separation at a given moment. Separation must be perfect if redissolution of pyridines from the sludge when washing with water is to be avoided. Pyridines are known strongly to influence the color stability of the finished product. Further, odor, doctor test and the acidity and alkalinity of the final product depend on proper separation of the sludge. Limitation of the contact time reduces sulfonation, and in consequence also troubles with emulsification during neutralization. After a short reaction time, without contact with air, the acid sludge is perfectly fluid, which makes it possible to employ two-stage countercurrent operation. The acid still present in the sludge after the initial contact is thus used for further action on the fresh raw benzole, instead of being used up in chemical reactions in the sludge itself.

Below are given typical results for treating raw benzole which distills between 82° C. and 225° C., with 80 percent over at 122° C. and 89.5 percent at 180° C. Specific gravity 0.892 at 15° C., sulphur content 2.47 percent. Refining with 2.35 percent by weight of sulphuric acid (95 percent) in a two-stage countercurrent plant with two minutes contact time in each stage, after water washing, neutralization and redistillation gave a raffinate which on the standard acid-wash test showed a discoloration of the acid layer, corresponding to the tint of a solution of 5 to 10 g potassium dichromate in 1000 ml. of a mixture of 50 percent by volume pure sulphuric acid and 50 percent by volume distilled water ("acid index" = 0.5 — 1.0). Treating losses were 0.6 percent. Refining with 4.5 percent by weight of sulphuric acid (95 percent) under otherwise unchanged conditions gave an acid index of 0.0 — 0.3. Losses were 1.18 percent. The sulphur content was reduced in the first case to 0.77 percent, and to 0.26 percent in the second case.

Comparing these figures with results obtained with the conventional batch treatment (in this particular case with Siry-Chamon agitators) it was found, when working to the same qualities of raffinate, that, with the bath agitators the acid consumption was 50 to 150 percent higher, with losses running from 50 to 150 percent higher. Good results have also been obtained from two-stage countercurrent operations and controlled contact time, when treating narrow fractions, as shown by Table I.

From a study of the literature on the refining of light shale oil fractions, obtained either by retorting of shale or by cracking crude shale oil, it can be

TABLE 1

Raw Product	% Acid By Weight	Refining Loss	"Acid Index"
Fraction boiling from 75 to 105° C	1.5	0.42	0.5–1.0
(Including forerunnings)	3.2	1.72	0.0–0.3
Fraction boiling from 80 to 105° C	1.5	0.70	0.3–0.5
(Excluding forerunnings)	2.7	0.97	0.0–0.3

concluded that sulphuric-acid treatment, combined with caustic-soda washing, and in most cases plumbite treatment has proved to be the most satisfactory method of procedure.[12] The Newnes investigation committee considered various methods of refining spirit from Australian shale oil, and concluded that, for the preparation of finished spirit conforming to the Australian standards, there was no alternative to the sulphuric-acid and caustic-soda method. The cost of refining by hydrogenation is reported to be prohibitive.[13] Both the chemical and the economic aspects are thoroughly discussed in the literature. It may be added here that the situation is very similar to that met with in dealing with low-temperature carbonization spirits, and the observations reported on that subject earlier in this paper apply also to shale gasoline.

In this field, too, experimental work has been carried out with the object of overcoming certain drawbacks of sulphuric-acid refining and of fully profiting by its advantages by thoroughly controlling refining conditions. The first commercial result was a continuous countercurrent plant with centrifugal separation for treating shale-oil distillate from retorts, in Esthonia in 1938. Two years later another plant of that type, with some minor improvements, was installed for handling Australian shale distillate obtained by thermal cracking in a Dubbs plant. During the recent world conflict, a plant was built which made it possible to produce motor fuel and aviation base stock from Swedish shale oil. In view of the necessary drastic refining, especially in the case of aviation base stock, particularly close control of all the variables of reaction was provided for. A series of pilot-plant tests has preceded the designing of each particular plant.

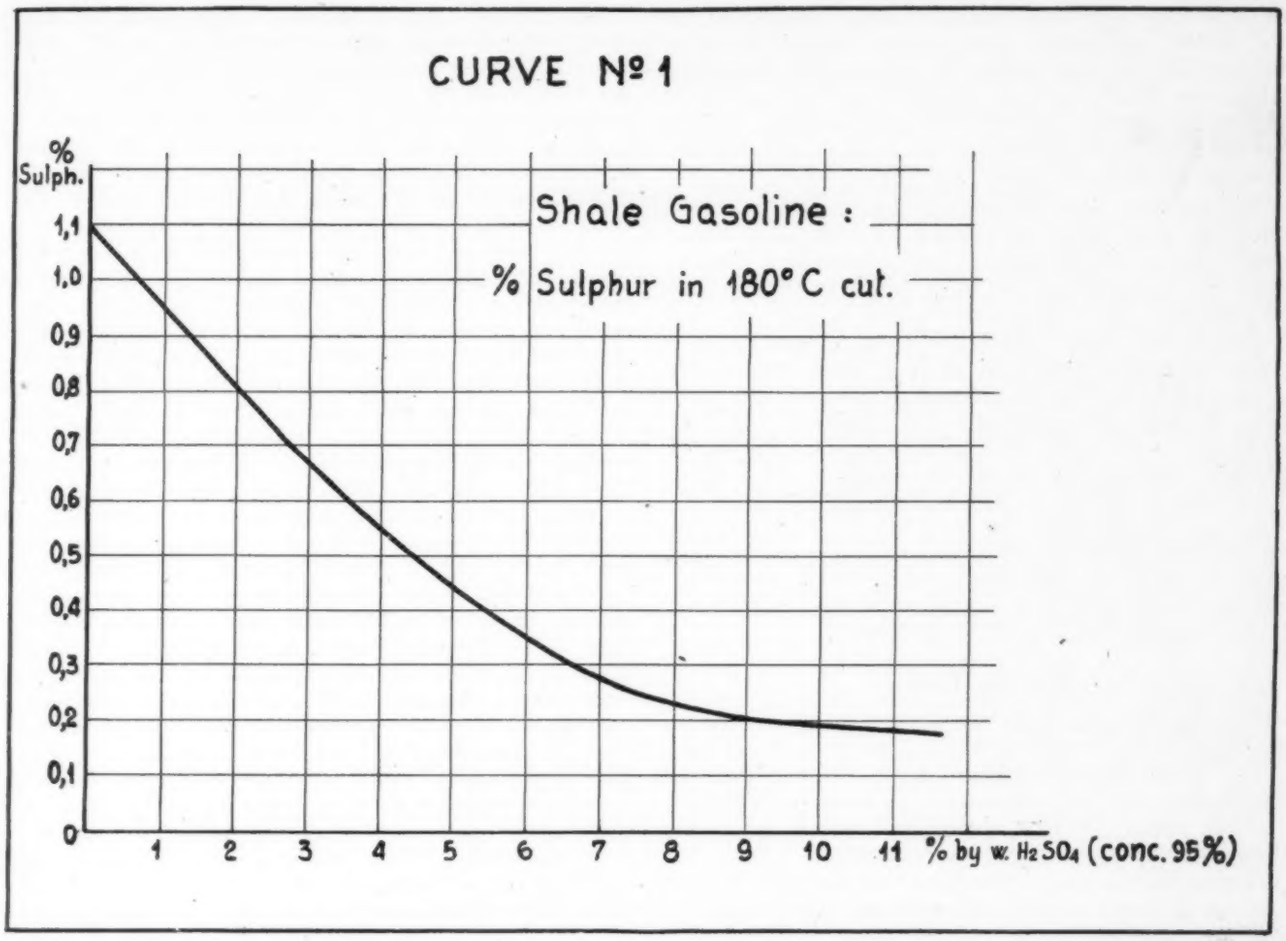

Table II presents a comparison between plant data from a discontinuous agitator plant in Esthonia and the two-stage countercurrent continuous centrifugal plant referred to earlier. The raw gasoline obtained partly by direct condensation, partly by topping a shale distillate from tunnel ovens, had the following properties:

Specific Gravity	0.760
I. B. P.	41° C.
at 100° C.	33 Percent over
at 175° C.	86 Percent over
at 200° C.	95 Percent over
F. B. P.	205° C.
sulphur, total	0.90 Percent
sulphur in 175° C. cut	0.81 Percent

Some figures are given here to show the action of sulphuric acid on the sulphur compounds of Dubbs-cracked Australian-shale gasoline. The raw pressure distillate, with a specific gravity of 0.750 and a sulphur content of 0.28 percent when treated with 2.6 percent by weight of acid (93 percent) by agitation, followed by gravity settling, yielded a

TABLE II

	Discontinuous Agitator Plant per cent	Continuous Centrifugal Plant per cent
Weight of sulphuric acid used	3.3	2.0
Concentration of acid	85	95
Refining losses	5.4	2.5
Sulphur in 175° C., cut	0.45	0.45

finished product with 0.19 percent sulphur after neutralization and redistillation. The same pressure distillate refined in a continuous countercurrent centrifugal plant with 1.9 percent by weight of acid (95 percent) yielded a product with 0.16 percent sulphur after the usual finishing operation.

Curve No. 1 shows the relation between the amount of sulphuric acid used in refining and the percent of sulphur in the 180° C. cut of the treated gasoline for a certain type of Swedish shale-oil distillate, all the other operating conditions being identical throughout the test series. As previously found for petroleum distillates with a high sulphur content,[15] prolonging the contact of acid and distillate over a certain limit only increased the losses, without improving desulphurization.

The primary aim of temperature control was to check the exothermic heat of reaction to avoid vapor losses. As to the chemical aspect, there is a definite optimum temperature for each problem. Below this temperature reaction is incomplete, while acid and hydrocarbons react above this temperature in such a way as to give relatively great hydrocarbon losses for a certain desired desulphurization. For the problems studied this optimum temperature was well above 0° C. It might be added here, as a matter of interest, that in the above described Swedist plant the so-called methanol-soda process (known from the benzol industry as a batch method for removing carbon disulphide[11,14] has been used for the first time, with the help of centrifugal separation, as a continuous refining process, its object, also in this case, being the removal of carbon disulphide

Refining Losses

The figures given for refining losses throughout this paper refer only to the losses of hydrocarbons to the acid, usually called solution losses. For the sake of simplicity no figures have been included for the "shrinkage." It is generally known that this phenomenon, also called polymerization loss, increase as the treating conditions become more drastic and can be largely reduced by proper operating control.[15] Vapor losses and the losses occuring during the water washing and the neutralization and the eventual formation of emulsions are to an even greater extent dependent on the mode of treatment. In plants with proper means for controlling operating conditions these losses are negligible but they vary widely for the older type of equipment and often even within the same plant, for various secondary reasons, and therefore they are not considered here in detail.

Throughout the progress of the work outlined in this paper, it has been attempted to progressively inhibit the chemical action of the sulphuric acid on the hydrocarbons and to take more advantage of its properties as a physical refining agent. While at first attention was directed chiefly on the refining operation as such, it soon became clear, in connection with the regeneration of acid sludge, that the reactions occuring in the acid sludge after separation from the raffinate also called for close attention. While the acid sludge resulting from treating hydrocarbon mixtures with even a relatively small percentage of unsaturated compounds, in plants of the older type, was mostly rather viscous, and sometimes even solid, the sludges from controlled refining operations, even when highly olefinic products are treated, is at first quite fluid. The acidity of the sludge, which was very low in the plants of the old type, could, in the case of controlled treatment be as high as 80 percent, expressed as sulphuric-acid equivalent. Owing to the continuation of the reactions in the freshly formed sludge—whether in contact with the bulk of raffinate or not—its qualities change more or less rapidly, all depending on the type of raw stock treated. In order to take full advantage of the improved refining conditions it was soon found necessary to split the acid sludge immediately after its separation from the raffinate, into hydrocarbons and sulphuric acid, by one of the known methods. Thus practically all the hydrocarbons are recovered, with a boiling range not very different from that of the raw material treated, as well as most of the treating agent, which, after undergoing an operation of concentration and after eventually receiving an addition of oleum, can be returned to the operating cycle.

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Basic Petroleum Chemistry For Refinery Employes

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Chapter IV
CHANGING THE STRUCTURE OF PETROLEUM MOLECULES

THERE are not many raw materials that are consumed in the same physical or chemical condition in which they are found in nature. Aluminum, for instance, is found in a number of forms chiefly as the hydrated oxide called bauxite. Iron is found in nature also in a variety of chemical combinations, but chiefly as an oxide of iron commonly called hematite. Magnesium too is found in forms called magnesite, dolomite, epsom salts and others. Even when used in the form in which they are found, most natural products require some physical or chemical change before they are of much useful value. Petroleum is no exception.

Prior to 1859 and drilling of the first oil well in this country, lamp oil had been prepared by distillation of coal. Hence, the name "coal oil." Sperm oil from whales was becoming expensive and difficult to buy, so the public was much interested in any endeavor which promised an abundant supply of illuminating oil. The production of coal oil from coal, gave way rather suddenly, to the distillation of a suitable product from petroleum following the rapid expansion of the oil industry.

Simple distillation was the chief method of refining until a few decades ago when a number of special refining processes became known and were developed for commercial use.

Before the automobile began to demand large quantities of fuel the light hydrocarbons boiling below kerosine had little or no utility. As a matter of fact, they actually constituted a serious waste-disposal problem. By 1910, these light hydrocarbons for automotive fuel were in greater demand than other petroleum fractions, and efforts were being made to increase the yield of gasoline from a barrel of crude oil. The answer was found in cracking processes which converted high-molecular-weight, high-boiling-point hydrocarbons into fractions suitable for automotive fuel.

Thermal Cracking

History does not fully substantiate the story that cracking was discovered accidentally by an incompetent stillman who forgot to open a valve in the vapor line of his batch still. As the story goes, he banked the fire under the still after charging it with crude oil. He then fell asleep while the oil was approaching its boiling temperature. He awakened in time to prevent a sudden and torrid trip to meet his maker. The temperature was beyond the boiling point of the crude and the pressure on the pot still was at the incipient bursting point. The distillate which came from the still after the vapor line was opened was of lighter nature and greater volume than ever before experienced. Thus was born the cracking process.

A hundred years before there developed a need for a process that would increase the yield of gasoline from crude oil, John Dalton, who formulated the fundamental concepts of the atomic theory (Chapter I), had found in 1809 that large hydrocarbon molecules could be decomposed into two or more molecules of lower molecular weight. By 1871, such other eminent scientists as Michael Faraday and Pierre Berthelot[1] had contributed to the knowledge which has become known as the "cracking art."

The term "cracking art" has come by usage to mean not only the knowledge concerning the breaking down of large molecules into smaller ones but also the technology of producing "tailor-made" molecules to meet specific needs.

The years following 1906 saw a flood of patent literature covering novel methods of producing motor fuel. It was beginning to be thought that the supply of crude oil was rapidly approaching exhaustion. No less authority than the National Geographic Survey was contributing much to the premature apprehension. The resulting increase in petroleum research gave birth to the first commercial cracking processes.

Under the influence of elevated temperatures and pressures for optimum periods of time, long-chain molecules "whip off" their extremities, producing two or more molecules of lower molecular weight and lower boiling point. Molecules of oil in a cracking furnace are in motion at such a high rate of speed that their ends or side chains are cracked off in a manner suggestive of the end fellow in a chain of boys playing "crack-the-whip." Similarly, long-chain molecules do not break apart in the middle of the

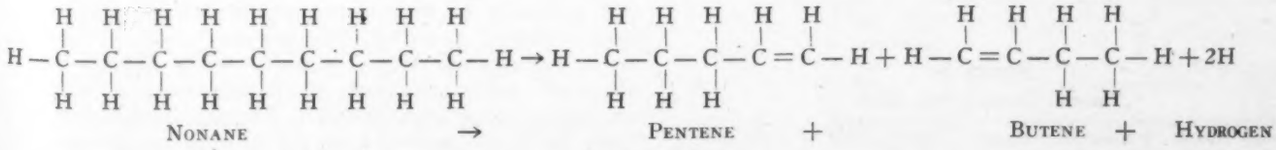

FIGURE 1

chain, consequently, light gases containing fewer than five carbon atoms are always produced to some extent from thermal cracking operations. Hydrogen and free carbon also are produced to some extent, depending upon operating conditions.

In Figure 1 is represented a possible break which might be expected to take place in a molecule of nonane.

As the length of the hydrocarbon chain increases, the ratio of hydrogen to carbon decreases. Consequently, when we make two shorter chains as above in Figure 1, there is created a deficiency of hydrogen to satisfy the four bonds of each carbon, resulting in the formation of olefins or unsaturated hydrocarbons such as pentene and butene.

Since unsaturates are relatively reactive, it is possible for the pentenes to recombine with hydrogen to form a heavier molecule than the original nonane as indicated by Figure 2.

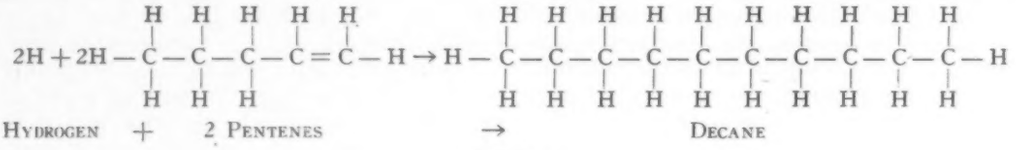

FIGURE 2

While decane is within the boiling range of gasoline we would not want to facilitate the reaction represented above because of the resulting depreciation of octane value. Decane has an octane value of —53R while pentene has a value of + 92R. Decane boils at 345° F. while pentene boils at 86° F.

Certain cracking stocks are high in compounds which unite progressively under the influence of cracking conditions to produce tar or asphaltic substances. Such reactions, as well as the one represented in Figure 2, are referred to as polymerization reactions. They proceed to some extent in all thermal cracking operations resulting in coke deposits which have to be cleaned from the furnace tubes. Such reactions in thermal cracking cannot be eliminated, but they can be controlled within limits. In order to prevent reactions of the type represented by Figure 2, the stock is held within the heated furnace tubes or reaction chamber (see Figure 3) just long enough to allow the cracking as represented by Figure 1, to take place. The hot oil is then cooled by introducing quench either at the furnace outlet, the reaction chamber outlet or both simultaneously. The oil from the reaction chamber is then separated from the vapors by means of an evaporator. The heavy-oil fraction contains hydrocarbon compounds on the verge of depositing coke, therefore, except for a small quantity used as quench, this heavy residuum fraction is withdrawn from the system through a heat exchanger and used as fuel or as raw material for the production of asphalt materials. The evaporator overhead is further separated into a light and intermediate fraction. The intermediate fraction containing uncracked molecules is called recycle stock and is recycled through the furnace tubes with the fresh charge. The light fraction overhead from the fractionator passes through a heat exchanger, a condenser, and finally a separator where the gas is separated from the gasoline. Although there are many deviations in cracking processes, the steps mentioned here are a part of practically all patented processes.

Thermal-cracking plants do not always employ reaction chambers, or soaking and coking chambers as they are sometimes called. However, research work conducted by Standard Oil Company of California[2] show that reaction chambers are of specific value for increasing the degree of cracking possible, decreasing the coke formation in the heater tubes, increasing the quality of the gasoline as to both octane value and volatility, increasing the quality of residuum by virtue of lower sediment content, and for increasing the overall capacity of the cracking unit. If coke is a desired by-product of the cracking process, coking chambers are, of course, necessary.

The first commercially successful cracking processes were those patented by William M. Burton (1913) and W. F. Rittman (1915)[3].

The thermal cracking operations are usually subdivided into two groups which are known as liquid-phase and vapor-phase processes. The liquid-phase, as the name implies, refers to the processes in which the cracking takes place while the oil is in the liquid state, usually at temperatures of 850° F. to 1000° F. and at pressures in excess of 1000 pounds per square inch. On the other hand, vapor-phase refers to the processes in which reaction takes place while the oil is completely vaporized. Hence, naphtha, kerosine and light gas oils are the most desirable charging stock. The temperatures employed in vapor-phase cracking are somewhat higher than in the liquid-phase operation, 1000° F. to 1500° F., however, the pressures employed are much lower—from 50 to 150 pounds per square inch. This lower pressure, of course, permits the hydrocarbons to exist as vapors in the cracking zone of the equipment.

Improvements in the gasoline engine, particularly increase in compression ratio, placed upon refiners the necessity of increasing anti-knock properties of their finished gasoline. The property was measured in a number of ways, usually with benzol as a standard reference fuel, until the use of octane-number became standardized. The standard reference fuels are now normal heptane having an arbitrarily assigned value of 0, and 2, 2, 4, trimethyl pentane

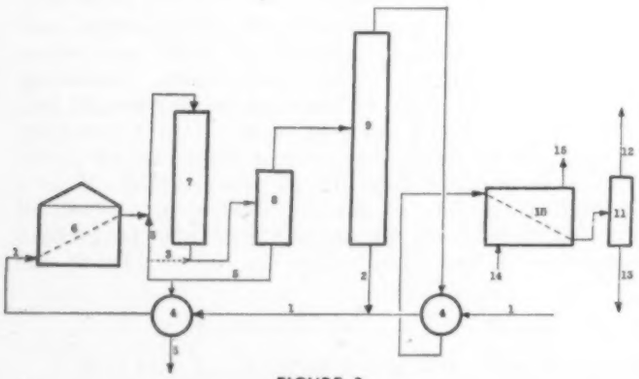

FIGURE 3

Thermal Cracking Flow Sheet

1 Charge; 2 Recycle; 3 Quench; 4 Heat Exchangers; 5 Residuum; 6 Tube Heater; 7 Reaction Chamber; 8 Evaporator; 9 Fractionator; 10 Condenser; 11 Separator; 12 Gas; 13 Gasoline; 14 Water Inlet; 15 Water Outlet.

having an arbitrarily assigned value of 100. Values between 0 and 100 are obtained by blending the two standards. Thus a blend of 72 percent 2, 2, 4, trimethyl pentane (which is an octane) and 28 percent normal heptane would be a 72-octane reference fuel. A gasoline matching it in knock intensity would be said to have an octane value of 72.

The vapor-phase cracking processes are capable of yielding a higher-octane-value gasoline than is possible by means of liquid-phase operations. The higher octane is attributed to the formation of aromatic hydrocarbon such as benzene, toluene, xylenes, ethyl benzene propyl and iso-propyl benzene and others, all of which have octane number values in the 100R-octane range. While aromatic hydrocarbons are also formed in liquid-phase operations, octane appreciation results largely from the change in structure of straight-chain molecules. In the thermal cracking operations, a multiplicity of reactions take place simultaneously. The reactions are generally classified under the terms: reforming, polymerization, isomerization, cyclization, aromatization, etc.

The hypothetical possibilities illustrated below in Figure 4 will indicate how octanes improve results from cracking operations.

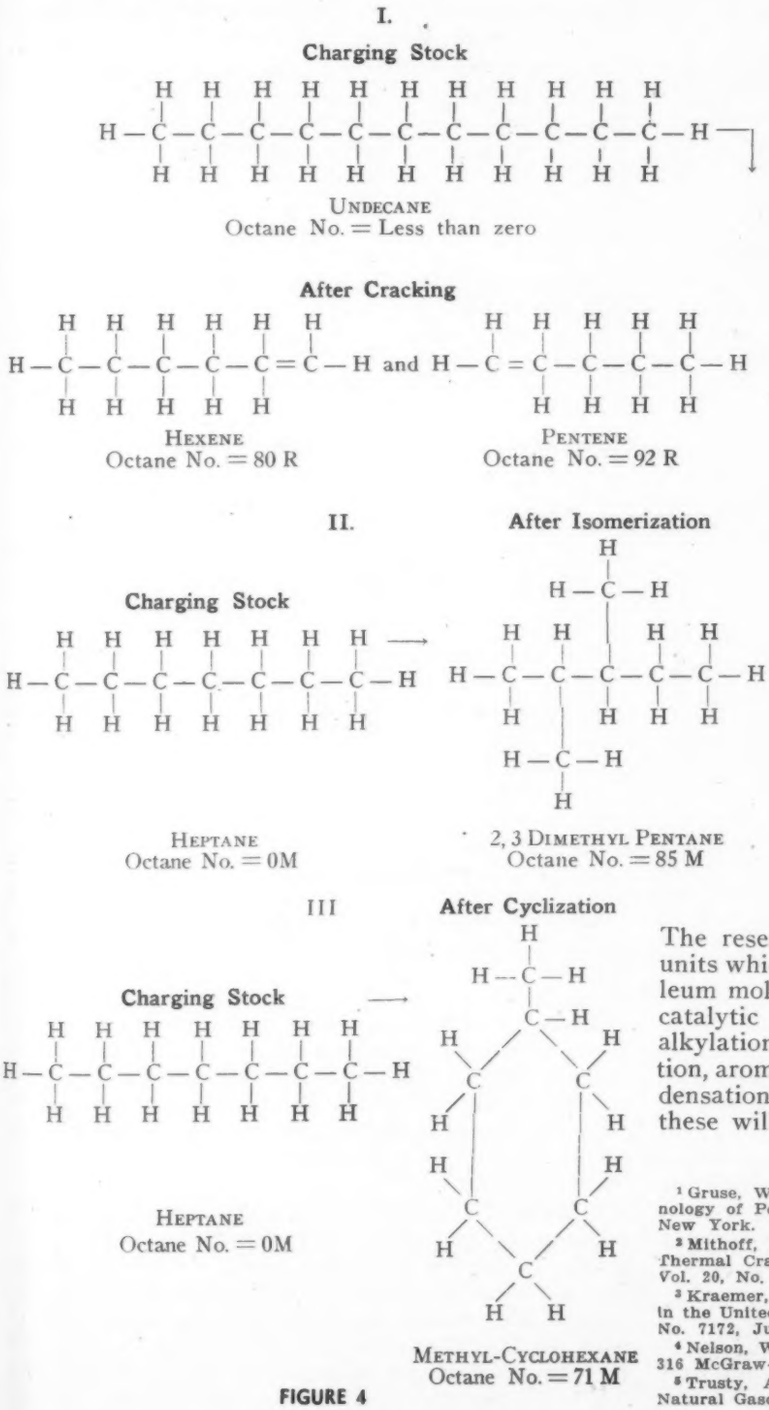

FIGURE 4

These are only a few type reactions which occur in cracking operations. By careful choice of equipment, charging stock and control of operating conditions, some degree of selection of the most desirable type of reaction is possible. A much higher degree of selection is possible with catalytic-cracking processes.

The cracking stocks available in refineries vary widely in both physical and chemical properties from light, low-octane naphthas to heavy fuel oils. It is sometimes desirable to know the approximate yield of 400-end-point gasoline which might be expected from a given charging stock. From a large number of commercial sets of data, the following equations were developed[4]:

Where A_S = API gravity of cracking stock
A_T = API gravity of cracked residue
S = Specific gravity of cracking stock

(1) % 400-end-point gasoline from gasoil or fuel oil $= 25 + 1.5\ (A_s - A_T)$

(2) % 400-end-point gasoline from coking fuel oil $= 300 - 250S$

(3) % 400-end-point gasoline from coking gas oil $= 331 - 300S$

(4) % gas and unaccounted-for losses $= 0.45\ (A_s - A_T)$

A high degree of accuracy should not be expected of these equations in all cases. They should be considered as furnishing approximate values only.

The critical solution temperature in C.P. anhydrous aniline, more commonly known as the aniline number is also a useful laboratory test in evaluating cracking and recycle stock.[5]

During the past 10 years much research work has been done in the field of changing the structure of petroleum molecules. The research has given birth to large commercial units which are doing specific structural jobs to petroleum molecules. The jobs they do are referred to as catalytic cracking, isomerization, polymerization, alkylation, dehydrogenation, hydrogenation, cyclization, aromatization, arylation, oxidative cracking, condensation and dealkylation. The more important of these will be discussed in the chapters that follow.

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Safe Practices for Air Compressor Operation

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ACCIDENTS seldom result from faults in the design of air compressors. Manufacturers realize that their equipment must be built to withstand variations in the load, speed, and pressure. These sudden changes often cause vibration and impose severe strain upon the foundation, flywheel, and other parts. Well designed air compressors compensate for these changes.

Few manufacturers, however, visualize the possibility of operators being injured by bodily contact with compressor belts, pulleys, flywheels, shafts, gears, and other moving parts. It is important, therefore, that adequate guards to enclose all moving parts should be installed.

Explosion Hazards

Severe explosions have occurred in compressed-air plants and few companies have avoided property damage or loss of life in mishaps at gasoline plants, gas-compressor stations or refineries. Investigation usually reveals that these accidents are due to certain malpractices or lack of information on the part of the operating personnel.

All causes of explosions in air compressors, receivers, and piping are not known, but authorities agree that attention must be given to proper lubrication, cleanliness of air at intake, air-cylinder temperature, and cooling of air between and after compressor stages, as well as correct piping.

Location and Foundation

A majority of air-compressor accidents result from improper installations as well as continued negligent operation and disregard for safety. An air compressor is looked upon by many engineers as a machine that can be shoved into an out-of-the way place and left to itself without further attention.

An air compressor requires regular inspection like any other piece of machinery and if the operator will spend a little time familiarizing himself with the practical principles, a big part of the trouble will be eliminated.

The compressor should be in a place that is clean and cool with ample space around the machine for cleaning, repairing, and inspecting. Boiler rooms, closed corners, and places where there is an absence of light or an accumulation of dust and dirt should be avoided.

All air compressors require a rigid foundation to minimize vibration. The foundation should be of good materials and well built. A mixture of one part cement, three parts coarse sand, and six parts broken stone is recommended. The foundation should stand at least a week after it is completed before placing the compressor upon it.

Capacities

A compressor should be chosen with full allowance for the requirements of the job it is to perform. It must be remembered that for an increase of 5°F. in the temperature of the intake air, a decrease of 1 percent in volumetric efficiency occurs, which means that as the intake-air temperature rises, the free-air capacity of the compressor decreases and the same amount of power is expended as though the full capacity of the compressor was being realized.

Compressor Lubrication

The proper amount of oil to be used in the air cylinder depends upon the viscosity of the oil, but the one safety factor to remember is that when the surface of the wall is once glazed over, little oil is required to maintain operation. The following table is valuable in determining the proper amount of oil required:

CYLINDER SIZE, INCHES	Cu. Ft. per Minute	Piston Speed—Ft. Per Minute	Sq. Ft. of Cyl. Wall Swept By Piston	Drops of Oil Per Minute Air Cylinder
6½x 6	57	330	440	1
8x 8	124	354	740	2
10x10	228	416	1095	2
12x12	371	470	1480	3
14x15	561	525	1930	4
16x15	730	525	2200	4
18x15	930	525	2480	5
20x15	1146	525	2770	6

Lubrication of the air cylinder, when incorrectly handled, is believed to be the one largest cause of explosions. The fact that the temperature of the air is increased considerably in the process of compression must be borne in mind. At a pressure as low as 100 pounds, the temperature of air cylinder often reaches 480°F., which is sufficient to vaporize certain grades of lubricating oil. When this vapor is mixed with air, an explosive mixture is formed that may be readily ignited by a glowing bit of carbon or by temperature alone.

Operators must be careful not to supply too much oil to air compressors. They require very little lubrication as there is no steam, water, or gas to absorb or wash away the oil film. The manufacturers' specifications are usually the most accurate gauges to be used. In the absence of this information, a good rule is 1 to 4 drops per minute for small compressors. Six drops per minute is usually sufficient for medium

sized, and 10 to 12 drops per minute for large compressors. If this quantity does not operate satisfactorily, there may be mechanical defects or perhaps the wrong grade of oil is being used. All conditions should be thoroughly checked to make certain that excessive lubrication is not taking place.

Decomposition of Oil

Explosion danger arises from burning, charring, or cracking of oil. Only high-grade mineral oil should be used that contains no animal or vegetable oil. Even the best oil decomposes to some extent and leaves a carbon deposit that is carried into the receiver and piping. This carbon deposit is flammable and soon becomes oil-soaked. It is under air pressure and exposed to great heat, so it may glow or burn, thus igniting any explosive mixture of oil vapor.

A deposit of this carbon may collect and build up at any point and become ignited and heat up a spot to such a high temperature that the point will rupture under pressure.

Carbon Deposits

There is also a possibility that a carbon deposit may be distributed to form a dust which may explode when mixed with air and ignited .

Faulty compressor discharge valves cause a sharp increase in air temperature as air churns back and forth and the friction alone may ignite carbon. Compressor valves should be cleaned at least once each month or oftener if service is continuous.

Some operators use 1 pound of soft soap in 7 or 8 quarts of water to clean carbon, and feed this into the cylinder about ten times faster than oil. Care must be taken to drain cylinder lines and receiver after treatment, and to operate the compressor for a short while with regular oil lubricant before beginning service.

In cases where carbon is hard and cannot be removed by soap or lye solution, it is necessary to scrape with a hand tool. Under no circumstances should kerosine, gasoline or any other flammable substance be used to soften carbon.

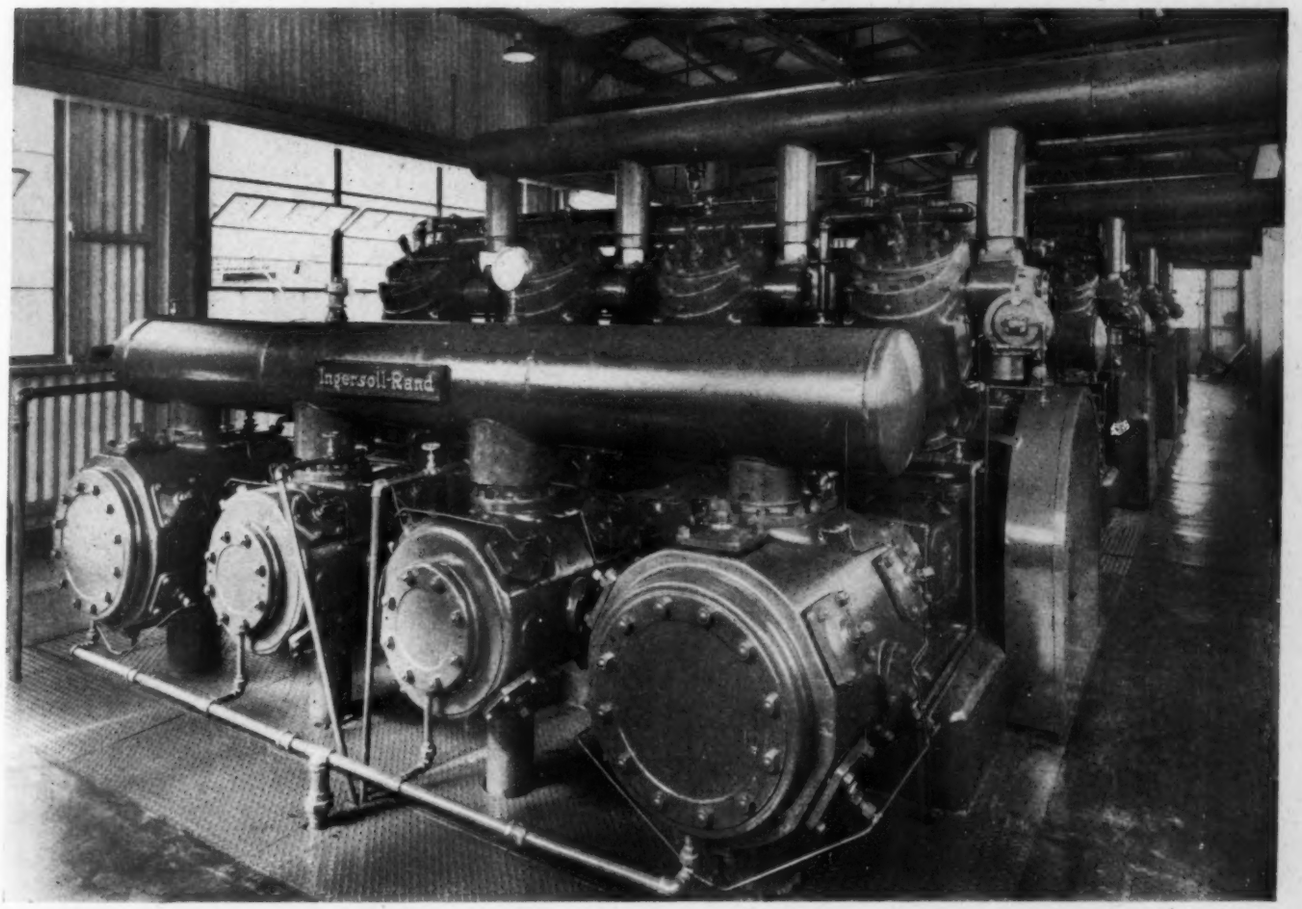
Clean Air at Intake

Explosions may occur by the ignition of flammable vapors drawn in at the intake. The intake, therefore, should be located where air is clean and cool. An air filter should also be installed.

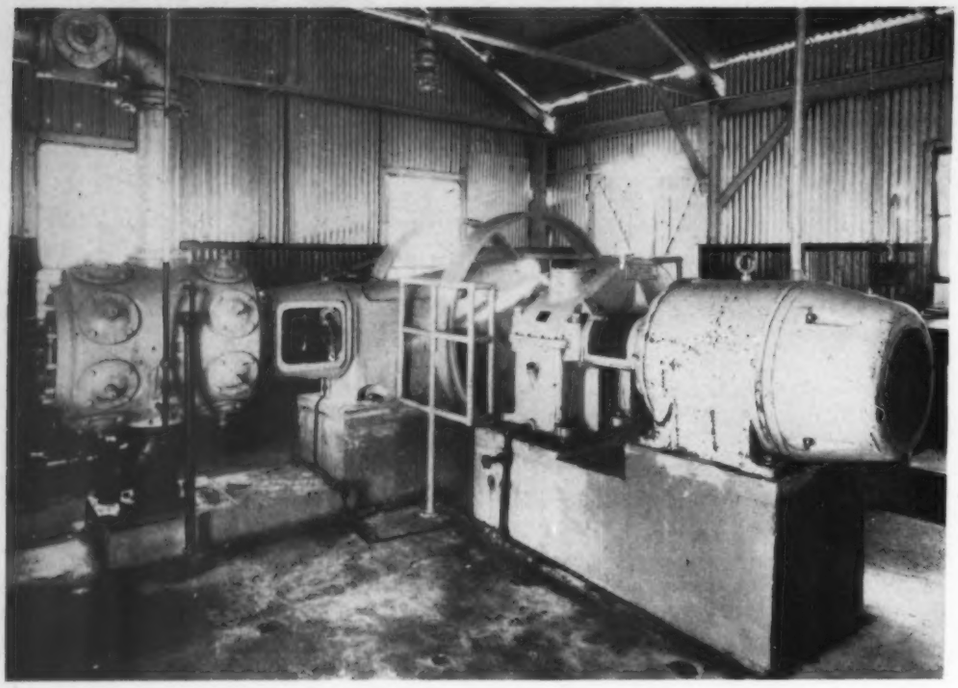
In case of gas, gasoline fumes, or rich vapor released near intakes, the compressor should be shut down.

The air-intake pipe should be some 8 or 10 feet above ground level, or above the roof, yet short and straight as possible to avoid pockets, turns, or traps where substances may accumulate. If the intake has such pockets; drains should be installed and checked daily. Moisture has little or no effect on fire or explosion danger but does cause a corrosive effect.

Every means should be used to keep the cylinder temperature down. This will decrease vaporization and decomposition of lubricating oil. This is accom-



Gas-engine-driven compressors



Motor-driven air compressor

plished by keeping ample cooling water circulating, drawing only cool, clean air into the cylinder, and operating the compressor at a speed no greater than recommended by the manufacturer.

Cooling Water

Deposits of scale form on the cylinder water jacket reducing the cooling effect of water. It is advisable to clean these jackets at least once a year. This can be done by a hot solution of caustic soda or some suitable substance.

A visible indication of water flow should be provided.

Fusible Plugs

Each air compressor should have a fusible plug in the discharge piping to relieve pressure or act as a whistle when the temperature exceeds a certain limit—perhaps fixed at 350 or 500°F., depending on the size of the compressor.

Discharge Piping

The discharge piping should be at least the diameter of the opening in the air cylinder and should be carried full size to the receiver. Bends, turns, and loops must be avoided as much as possible and the pipe preferably sloped to the receiver.

Air Receivers

The function of a receiver is to create a cushion and eliminate pulsation; serve as a storage of power; cool air and precipitate oil or moisture in entrainment; and eliminate friction losses that would occur, if cooling were effected in the piping.

The receiver should be as close as possible to the compressor and in a cool place. Installations on or under ground near compressors, engines, or hot points are to be strictly avoided as radiation may cause temperature rise. The receiver should be located so that it can be inspected on all sides.

Each receiver should have a pressure gauge, safety valve, and blow-off cock.

A shut-off valve should never be placed between the compressor and the receiver unless a safety valve is placed on the compressor side of the valve.

The air outlet from the receiver should be from the top.

Working Pressures

All piping, fittings, and equipment must be of a test pressure at least 1½ times the normal operating pressure.

Air receivers are subject to state, federal and insurance code requirements and must be tested to 1½ times their working pressure and should be constructed according to ASME Code.

Air-Starting Piping

Air-starting piping should run full size as straight and short as possible with the minimum of turns, bends, or pockets.

Air-starting lines should have 2 check valves located at least 10 pipe diameters apart. In case of engine backfire, glowing carbon may be blown past a single check and ignite flammable vapors present in the air receiver and piping.

An adequate drain should be installed on air-starting piping below receiver level and blown daily or before each engine starting to eliminate water, scale or emulsion.

Provision should be made for piping expansion and contraction, and overhead lines eliminated, if possible.

Personal Protective Devices

The use of goggles, respirators, or screens is necessary to protect the eyes of operators and nearby workmen when compressed air is used to drive tools, paint sprays, etc.

General

Many injuries have resulted from practical joking by "goosing" a worker with an air hose causing air to inflate the bowels until they burst.

Operators have been known to direct the air hose at themselves or each other blow dust out of clothing or for the pleasant cooling sensation. Such practice has injured eyesight and hearing, as well as killed men.

The use of compressed air to clean engines, buildings, etc., is dangerous. Often compressed air has vaporized oil to such an extent that it is highly explosive and the release of quantities of it near a source of ignition may cause an explosion.

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195	—5.4	—4.5	—3.5	—2.6	—17	—0.7	0.2	1.2	2.1	3.0	3.9	4.8	5.7	6.6	7.5	8.4	9.3
196	—5.4	—4.5	—3.6	—2.7	—18	—0.8	0.2	1.1	2.0	2.9	3.9	4.8	5.7	6.6	7.5	8.4	9.3
197	—5.5	—4.6	—3.6	—2.7	—18	—0.8	0.2	1.1	2.0	2.9	3.8	4.7	5.6	6.5	7.4	8.3	9.2
198	—5.5	—4.6	—3.7	—2.8	—18	—0.9	0.1	1.0	1.9	2.8	3.8	4.7	5.6	6.5	7.4	8.3	9.2
199	—5.6	—4.7	—3.7	—2.8	—19	—0.9	0.1	1.0	1.9	2.8	3.7	4.6	5.5	6.4	7.3	8.2	9.1
200	—5.6	—4.7	—3.7	—2.8	—19	—1.0	0.0	0.9	1.8	2.7	3.7	4.6	5.5	6.4	7.3	8.2	9.1
201	—5.6	—4.7	—3.8	—2.9	—19	—1.0	0.0	0.9	1.8	2.7	3.6	4.5	5.4	6.3	7.2	8.1	9.0
202	—5.7	—4.8	—3.8	—2.9	—20	—1.0	0.0	0.9	1.8	2.7	3.6	4.5	5.4	6.3	7.2	8.1	9.0
203	—5.7	—4.8	—3.9	—2.9	—20	—1.1	—0.1	0.8	1.7	2.6	3.6	4.5	5.4	6.3	7.2	8.1	9.0
204	—5.8	—4.9	—3.9	—3.0	—20	—1.1	—0.1	0.8	1.7	2.6	3.5	4.4	5.3	6.2	7.1	8.0	8.9
205	—5.8	—4.9	—3.9	—3.0	—21	—1.2	—0.2	0.7	1.6	2.5	3.5	4.4	5.3	6.2	7.1	8.0	8.9
206	—5.9	—4.9	—4.0	—3.1	—21	—1.2	—0.2	0.7	1.6	2.5	3.4	4.3	5.2	6.1	7.0	7.9	8.8
207	—5.9	—5.0	—4.0	—3.1	—22	—1.2	—0.3	0.6	1.5	2.4	3.4	4.3	5.2	6.1	7.0	7.9	8.8
208	—5.9	—5.0	—4.1	—3.1	—22	—1.3	—0.3	0.6	1.5	2.4	3.3	4.2	5.1	6.0	6.9	7.8	8.7
209	—6.0	—5.1	—4.1	—3.2	—23	—1.3	—0.3	0.6	1.5	2.4	3.3	4.2	5.1	6.0	6.9	7.8	8.7
210	—6.0	—5.1	—4.1	—3.2	—23	—1.4	—0.4	0.5	1.4	2.3	3.2	4.1	5.0	5.9	6.8	7.7	8.6
211	—6.1	—5.1	—4.2	—3.2	—23	—1.4	—0.5	0.5	1.4	2.3	3.2	4.1	5.0	5.9	6.8	7.7	8.6
212	—6.1	—5.2	—4.2	—3.3	—24	—1.5	—0.5	0.4	1.3	2.2	3.2	4.1	5.0	5.9	6.8	7.7	8.5
213	—6.1	—5.2	—4.3	—3.3	—24	—1.5	—0.6	0.4	1.3	2.2	3.1	4.0	4.9	5.8	6.7	7.6	8.5
214	—6.2	—5.3	—4.3	—3.4	—25	—1.6	—0.6	0.3	1.2	2.1	3.1	4.0	4.9	5.8	6.7	7.6	8.4
215	—6.2	—5.3	—4.4	—3.4	—25	—1.6	—0.7	0.3	1.2	2.1	3.0	3.9	4.8	5.7	6.6	7.5	8.4
216	—6.2	—5.3	—4.4	—3.5	—26	—1.6	—0.7	0.2	1.1	2.0	3.0	3.9	4.8	5.7	6.6	7.5	8.3
217	—6.3	—5.4	—4.5	—3.5	—26	—1.7	—0.7	0.2	1.1	2.0	2.9	3.8	4.7	5.6	6.5	7.4	8.3
218	—6.3	—5.4	—4.5	—3.6	—26	—1.7	—0.8	0.1	1.1	2.0	2.9	3.8	4.7	5.6	6.5	7.4	8.2
219	—6.3	—5.4	—4.5	—3.6	—27	—1.8	—0.8	0.1	1.0	1.9	2.9	3.7	4.6	5.5	6.4	7.3	8.2
220	—6.4	—5.5	—4.6	—3.7	—27	—1.8	—0.9	0.0	1.0	1.9	2.8	3.7	4.6	5.5	6.4	7.3	8.1
221	—6.4	—5.5	—4.6	—3.7	—28	—1.8	—0.9	0.0	0.9	1.8	2.8	3.6	4.5	5.4	6.3	7.2	8.1
222	—6.5	—5.6	—4.7	—3.8	—28	—1.9	—0.9	0.0	0.9	1.8	2.7	3.6	4.5	5.4	6.3	7.2	8.0
223	—6.5	—5.6	—4.7	—3.8	—29	—1.9	—1.0	—0.1	0.8	1.7	2.7	3.5	4.4	5.3	6.2	7.1	8.0
224	—6.5	—5.6	—4.7	—3.8	—29	—2.0	—1.0	—0.1	0.8	1.7	2.6	3.5	4.4	5.3	6.2	7.1	7.9
225	—6.6	—5.7	—4.8	—3.9	—29	—2.0	—1.1	—0.2	0.8	1.7	2.6	3.5	4.3	5.2	6.1	7.0	7.9
226	—6.6	—5.7	—4.8	—3.9	—30	—2.0	—1.1	—0.2	0.7	1.6	2.5	3.4	4.3	5.2	6.1	7.0	7.8
227	—6.7	—5.8	—4.9	—4.0	—30	—2.1	—1.1	—0.2	0.7	1.6	2.5	3.4	4.3	5.2	6.0	6.9	7.8
228	—6.7	—5.8	—4.9	—4.0	—31	—2.1	—1.2	—0.3	0.6	1.5	2.5	3.3	4.2	5.1	6.0	6.9	7.7
229	—6.7	—5.8	—4.9	—4.0	—31	—2.2	—1.2	—0.3	0.6	1.5	2.4	3.3	4.2	5.1	6.0	6.8	7.7
230	—6.8	—5.9	—5.0	—4.1	—31	—2.2	—1.3	—0.4	0.5	1.5	2.4	3.2	4.1	5.0	5.9	6.8	7.6

A.P.I. HYDROMETER INDICATION TABLE—HIGH-TEMPERATURE EXT

11	12	13	14	15	16	17	18	19	20	21	22	23	24	2
4.8	5.7	6.6	7.5	8.4	9.3	10.2	11.1	12.0	12.9	13.8	14.7	15.6	16.5	1
4.8	5.7	6.6	7.5	8.4	9.3	10.2	11.1	11.9	12.8	13.7	14.6	15.5	16.4	1
4.7	5.6	6.5	7.4	8.3	9.2	10.1	11.0	11.9	12.8	13.7	14.6	15.5	16.4	1
4.7	5.6	6.5	7.4	8.3	9.2	10.1	11.0	11.8	12.7	13.6	14.5	15.4	16.3	1
4.6	5.5	6.4	7.3	8.2	9.1	10.0	10.9	11.8	12.7	13.6	14.5	15.4	16.3	1
4.6	5.5	6.4	7.3	8.2	9.1	10.0	10.9	11.7	12.6	13.5	14.4	15.3	16.2	1
4.5	5.4	6.3	7.2	8.1	9.0	9.9	10.8	11.7	12.6	13.5	14.4	15.3	16.2	1
4.5	5.4	6.3	7.2	8.1	9.0	9.9	10.8	11.6	12.5	13.4	14.3	15.2	16.1	1
4.5	5.4	6.3	7.2	8.1	9.0	9.8	10.7	11.6	12.5	13.4	14.3	15.2	16.1	1
4.4	5.3	6.2	7.1	8.0	8.9	9.8	10.7	11.5	12.4	13.3	14.2	15.1	16.0	1
4.4	5.3	6.2	7.1	8.0	8.9	9.7	10.6	11.5	12.4	13.2	14.1	15.0	15.9	1
4.3	5.2	6.1	7.0	7.9	8.8	9.7	10.6	11.4	12.3	13.2	14.1	15.0	15.9	1
4.3	5.2	6.1	7.0	7.9	8.8	9.6	10.5	11.4	12.3	13.1	14.0	14.9	15.8	1
4.2	5.1	6.0	6.9	7.8	8.7	9.6	10.5	11.3	12.2	13.1	14.0	14.9	15.8	1
4.2	5.1	6.0	6.9	7.8	8.7	9.5	10.4	11.3	12.2	13.0	13.9	14.8	15.7	1
4.1	5.0	5.9	6.8	7.7	8.6	9.5	10.4	11.2	12.1	13.0	13.9	14.8	15.7	1
4.1	5.0	5.9	6.8	7.7	8.6	9.4	10.3	11.2	12.1	12.9	13.8	14.7	15.6	1
4.1	5.0	5.9	6.8	7.7	8.5	9.4	10.3	11.1	12.0	12.9	13.8	14.7	15.6	1
4.0	4.9	5.8	6.7	7.6	8.5	9.3	10.2	11.1	12.0	12.8	13.7	14.6	15.5	1
4.0	4.9	5.8	6.7	7.6	8.4	9.3	10.1	11.0	11.9	12.8	13.7	14.5	15.4	1
3.9	4.8	5.7	6.6	7.5	8.4	9.2	10.1	11.0	11.9	12.7	13.6	14.5	15.4	1
3.9	4.8	5.7	6.6	7.5	8.3	9.2	10.0	10.9	11.8	12.7	13.6	14.4	15.3	1
3.8	4.7	5.6	6.5	7.4	8.3	9.1	10.0	10.9	11.8	12.6	13.5	14.4	15.3	1
3.8	4.7	5.6	6.5	7.4	8.2	9.1	9.9	10.8	11.7	12.6	13.5	14.3	15.2	1
3.7	4.6	5.5	6.4	7.3	8.2	9.0	9.9	10.8	11.7	12.5	13.4	14.3	15.2	1
3.7	4.6	5.5	6.4	7.3	8.1	9.0	9.8	10.7	11.6	12.4	13.3	14.2	15.1	1
3.6	4.5	5.4	6.3	7.2	8.1	9.0	9.8	10.7	11.6	12.4	13.3	14.1	15.0	1
3.6	4.5	5.4	6.3	7.2	8.0	8.9	9.7	10.6	11.5	12.3	13.2	14.1	15.0	1
3.5	4.4	5.3	6.2	7.1	8.0	8.9	9.7	10.6	11.5	12.3	13.2	14.0	14.9	1
3.5	4.4	5.3	6.2	7.1	7.9	8.8	9.6	10.5	11.4	12.2	13.1	14.0	14.8	1
3.5	4.3	5.2	6.1	7.0	7.9	8.8	9.6	10.5	11.4	12.2	13.1	13.9	14.8	1
3.4	4.3	5.2	6.1	7.0	7.8	8.7	9.5	10.4	11.3	12.1	13.0	13.9	14.7	1
3.4	4.3	5.2	6.0	6.9	7.8	8.7	9.5	10.4	11.3	12.1	13.0	13.8	14.7	1
3.3	4.2	5.1	6.0	6.9	7.7	8.6	9.4	10.3	11.2	12.0	12.9	13.8	14.6	1
3.3	4.2	5.1	6.0	6.8	7.7	8.6	9.4	10.3	11.2	12.0	12.9	13.7	14.6	1
3.2	4.1	5.0	5.9	6.8	7.6	8.5	9.3	10.2	11.1	11.9	12.8	13.7	14.5	1

Compiled by John Griswold, The University of Texas, Austin, Texas

A.P.I. Hydrometer Indication Table—High-Temperature Extension

THE A.P.I. Hydrometer Indication Table given in *Bureau of Standard Circular 410* and the *Tag Manual* is discontinued at 195° F. for heavy oils. It is sometimes necessary or convenient to determine A.P.I. gravities at higher temperatures, particularly for viscous residual oils and asphalts.

The accompanying table extends the hydrometer corrections to 230° F. for oils of 0° to 39° A.P.I. This extension was calculated with the coefficients of expansion used in *Bureau of Standards Circulars 154* and *410*, for oils of Groups 0, 1, and 2, and includes the volumetric expansion of the glass hydrometer just as in the Bureau of Standards table. It will be found of sufficient accuracy for most purposes, the principal inaccuracy accruing from differences in coefficients of expansion of oils from different sources.

URE EXTENSION

24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	Observed Temperature in °F.
16.5	17.4	18.3	19.2	20.1	21.0	21.8	22.7	23.6	24.5	25.4	26.3	27.1	28.0	28.9	29.7	195
16.4	17.3	18.2	19.1	20.0	20.9	21.7	22.6	23.5	24.4	25.3	26.2	27.1	27.9	28.8	29.6	196
16.4	17.3	18.2	19.1	20.0	20.9	21.7	22.6	23.5	24.4	25.3	26.1	27.0	27.9	28.7	29.6	197
16.3	17.2	18.1	19.0	19.9	20.8	21.6	22.5	23.4	24.3	25.2	26.1	26.9	27.8	28.7	29.5	198
16.3	17.2	18.1	19.0	19.8	20.7	21.6	22.5	23.4	24.2	25.1	26.0	26.9	27.8	28.6	29.5	199
16.2	17.1	18.0	18.9	19.8	20.7	21.5	22.4	23.3	24.2	25.1	25.9	26.8	27.7	28.5	29.4	200
16.2	17.1	18.0	18.9	19.7	20.6	21.4	22.3	23.2	24.1	25.0	25.9	26.8	27.6	28.5	29.3	201
16.1	17.0	17.9	18.8	19.7	20.6	21.4	22.3	23.2	24.1	25.0	25.8	26.7	27.6	28.4	29.3	202
16.1	17.0	17.9	18.8	19.6	20.5	21.3	22.2	23.1	24.0	24.9	25.7	26.6	27.5	28.3	29.2	203
16.0	16.9	17.8	18.7	19.5	20.4	21.3	22.2	23.1	23.9	24.8	25.7	26.6	27.4	28.3	29.1	204
15.9	16.8	17.7	18.6	19.5	20.4	21.2	22.1	23.0	23.9	24.8	25.6	26.5	27.4	28.2	29.1	205
15.9	16.8	17.7	18.6	19.4	20.3	21.2	22.1	22.9	23.8	24.7	25.6	26.4	27.3	28.1	29.0	206
15.8	16.7	17.6	18.5	19.4	20.3	21.1	22.0	22.9	23.8	24.6	25.5	26.4	27.3	28.1	29.0	207
15.8	16.7	17.6	18.5	19.3	20.2	21.0	21.9	22.8	23.7	24.6	25.4	26.3	27.2	28.0	28.9	208
15.7	16.6	17.5	18.4	19.2	20.1	21.0	21.9	22.8	23.6	24.5	25.4	26.2	27.1	27.9	28.8	209
15.7	16.6	17.5	18.4	19.2	20.1	20.9	21.8	22.7	23.6	24.5	25.3	26.2	27.1	27.9	28.8	210
15.6	16.5	17.4	18.3	19.1	20.0	20.9	21.8	22.6	23.5	24.4	25.3	26.1	27.0	27.8	28.7	211
15.6	16.5	17.3	18.2	19.1	20.0	20.8	21.7	22.6	23.5	24.3	25.2	26.1	27.0	27.8	28.7	212
15.5	16.4	17.3	18.2	19.0	19.9	20.8	21.7	22.5	23.4	24.3	25.1	26.0	26.9	27.7	28.6	213
15.4	16.3	17.2	18.1	18.9	19.8	20.7	21.6	22.5	23.3	24.2	25.1	25.9	26.8	27.6	28.5	214
15.4	16.3	17.2	18.1	18.9	19.8	20.7	21.6	22.4	23.3	24.2	25.0	25.9	26.8	27.6	28.5	215
15.3	16.2	17.1	18.0	18.8	19.7	20.6	21.5	22.3	23.2	24.1	24.9	25.8	26.7	27.5	28.4	216
15.3	16.2	17.0	17.9	18.8	19.7	20.6	21.5	22.3	23.2	24.0	24.9	25.7	26.6	27.5	28.4	217
15.2	16.1	17.0	17.9	18.7	19.6	20.5	21.4	22.2	23.1	24.0	24.8	25.7	26.6	27.4	28.3	218
15.2	16.0	16.9	17.8	18.7	19.6	20.4	21.3	22.2	23.0	23.9	24.7	25.6	26.5	27.3	28.2	219
15.1	16.0	16.9	17.8	18.6	19.5	20.4	21.3	22.1	23.0	23.8	24.7	25.6	26.4	27.3	28.2	220
15.0	15.9	16.8	17.7	18.5	19.4	20.3	21.2	22.0	22.9	23.8	24.6	25.5	26.4	27.2	28.1	221
15.0	15.9	16.7	17.6	18.5	19.4	20.3	21.2	22.0	22.9	23.7	24.6	25.4	26.3	27.1	28.0	222
14.9	15.8	16.7	17.6	18.4	19.3	20.2	21.1	21.9	22.8	23.7	24.5	25.4	26.3	27.1	28.0	223
14.8	15.7	16.6	17.5	18.4	19.3	20.2	21.1	21.9	22.8	23.6	25.5	25.3	26.2	27.0	27.9	224
14.8	15.7	16.6	17.5	18.3	19.2	20.1	21.0	21.8	22.7	23.6	24.4	25.3	26.1	27.0	27.8	225
14.7	15.6	16.5	17.4	18.2	19.1	20.0	20.9	21.8	22.6	23.5	24.3	25.2	26.1	26.9	27.8	226
14.7	15.6	16.5	17.4	18.2	19.1	20.0	20.9	21.7	22.6	23.4	24.3	25.1	26.0	26.8	27.7	227
14.6	15.5	16.4	17.3	18.1	19.0	19.9	20.8	21.7	22.5	23.4	24.2	25.1	25.9	26.8	27.7	228
14.6	15.5	16.4	17.2	18.1	19.0	19.9	20.8	21.6	22.5	23.3	24.2	25.0	25.9	26.7	27.6	229
14.5	15.4	16.3	17.2	18.0	18.9	19.8	20.7	21.5	22.4	23.3	24.1	25.0	25.8	26.7	27.5	230

Relation of Octane Number And Peroxide Content of Catalytic Gasolines

DR. H. VELDE, Translated by E. J. BARTH, Petroleum Technologist

WHEN gasolines are kept in storage any length of time an unfortunate decrease in the octane number takes place, which is primarily due to the formation of peroxides. The latter are formed by the oxidation of the gasoline, which is measured by an increase in the so-called "peroxide-number." This oxidation has been referred to by a number of investigators, especially by Schildwachter in Germany[1] whose copious reports show how oxidation takes place, and what, if any, is the relation to the decrease in octane number. He describes how peroxide contents increase in storage. Other workers in this field have done much toward advancing our knowledge of this oxidation phenomenon. Since, for instance, in the case of Fischer-Tropsch gasoline, as in many other types, the material is chiefly of aliphatic constitution, and therefore is easily oxidized, the problem is especially important to us from synthetic angles, and for that reason we had embarked quite early upon a systematic program of thorough investigation in this direction. In the following discussion we will therefore report on some of our findings in our work on this subject—which deals, in the main, with the problem: how does peroxide formation and content affect the octane number.

As to analytical methods, the octane number was determined by the CFR-research method with a CFR motor or an I.G. test motor. The peroxide numbers are determined by the method of Yule and Wilson based on the investigations of Koch and Pohl.[2] Ten cc's of the benzine, containing peroxides, are customarily shaken with ferrous sulphate solution (thiocyanate as indicator) and the ferric salt formed is again reduced with titanium chloride solution. The results of the titration are according to the literature[2] corrected from a correction curve, and the calculated to oxygen using a correction-factor of 8. The peroxide number is then expressed as milligrams of oxygen per liter of gasoline. In general, we would dilute the test gasoline with some peroxide-free naphtha in order to hold down the quantity of titanium chloride to be used to below 3 cc. Good agreement of many determinations was obtained even with high-peroxide-content gasolines.

The following points are now under discussion and will be treated one by one:

(1) Light sensitivity of synthetic gasolines—how does octane number and peroxide content vary in presence of sunlight.

(2) Increase the peroxide content with drum storage.

(3) Quantitative relationship of octane number and peroxide number.

(4) Change in octane number by removing the peroxides.

1. Light Sensitivity of Synthetic Gasolines—Changes in Octane Number and Peroxide Contents by Light

The test procedure is quite simple. We selected a straight-run gasoline of about 160° C. endpoint, a vapor-phase-cracked stock, and a third grade which is a mixture of 1:1 of straight-run and cracked stock. These gasolines were placed in glass-stoppered flasks sealed fairly well. When the flasks were filled with the liquids the air was not displaced but a certain amount of air was present in all the tests. In order to obtain a comparison without sunlight we used regular and also brown-tinted glass flasks, and also another series of the same stored in the dark, away from light.

The results obtained are shown in tabular form in Tables 1 to 3, and in Figures 1 to 3. As we had expected, we note that the gasolines set out in light in the clear flasks show a rapid rise in peroxides with exposure time, while the brown flasks exposed to light show only a slight gain; the tests in shielded light (dark storage), especially those in the brown flasks, show only a trace of peroxide formation.

Parallel to these tests, which were merely to show changes in peroxides with time, we also exposed the three gasolines to four storage tests in sunlight. These samples were analyzed for peroxides and also for octane number. All other tests which are of extreme importance were also determined for all four tests on the three products. The results are shown in Tables 4 to 6.

The physical properties appear to have remained pretty well constant, as far as we went, while the octane value showed a large decrease, with neutralization showing an increase with increased time of storage. In addition we may add, as was shown by later tests, that the actual storage stability (such as by the oxidation-evaporation and bomb test) did not change in the case of the straight-run gasoline, even though it contained no inhibitor, and even though the peroxides had increased and octane number had diminished. In the case of the other two gasolines—mixed, and pure cracked oils—the expected relationships in this direction are not so favorable.

2. Increase of Peroxides with Time of Drum Storage

The same gasolines described above were placed and stored in 200-liter iron drums. To test the effect of various inhibitors the following substances were added to the oils: cresol 0.2 g. per liter; power alcohol 11.5 percent vol.; TEL 0.5 cc. per liter; and mixtures of these, such as alcohol plus cresol, TEL plus cresol, TEL plus alcohol and alcohol plus cresol plus TEL. The gasolines were tested at the

end of two years storage. The results of these extensive tests are shown in Tables 7 to 9.

In all cases the uninhibited gasoline showed large increases in the peroxide contents with corresponding decrease in octane number. The octane numbers in this case are not too exact since values lower than the original standard gasoline were difficult to determine. Qualitatively speaking, it is seen, nevertheless, that large and definite decreases in octane number had resulted.

The additions of these chemicals show at once some very surprising results. The anti-oxidant effect of cresol results in a remarkable stabilizing tendency, the octane number decreasing only a few points. With straight-run and mixed gasoline the power alcohol also acted as a good stabilizer, holding the octane number at a constant. With the cracked gasoline, the peroxides rose although the octane number did not drop off to a relatively high degree. With TEL additions, in the galvanized drum test, the

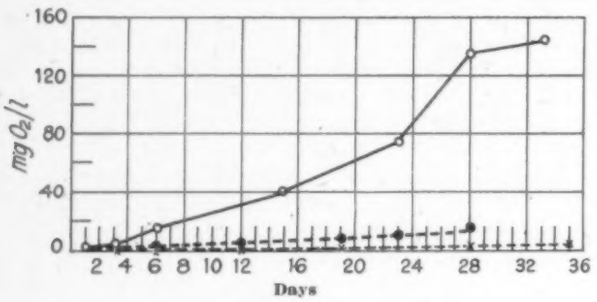

FIGURE 1

Increase in peroxide number with storage time for straight-run gasoline.

x———x Transparent flasks, covered.
o———o Transparent flasks, uncovered
x - - - - x Brown flasks, covered.
• - - - - • Brown flasks, uncovered.

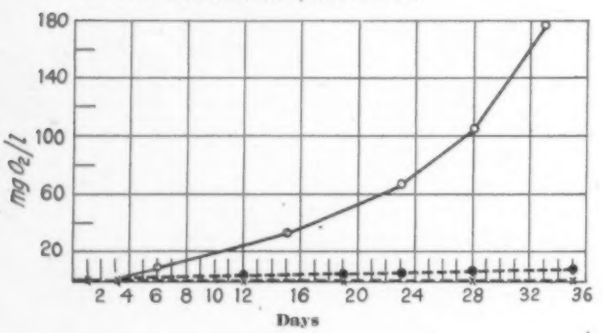

FIGURE 2

Increase in peroxide number with storage time for refined cracked gasoline.

(See Figure 1 for designation)

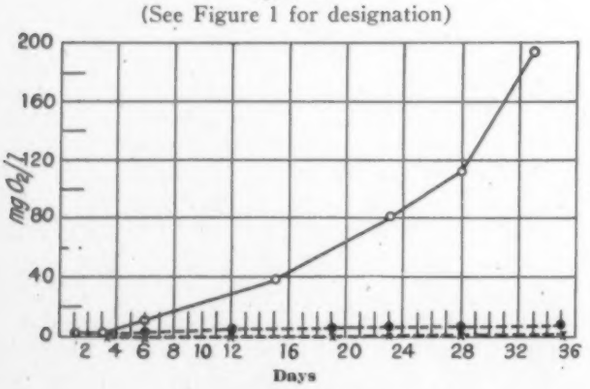

FIGURE 3

Increase in peroxide number with storage time for blended gasoline.

(See Figure 1 for designation)

TABLE 1

Change of Peroxide Content in Straight-Run Gasoline on Storage

STORAGE TIME DAYS	PEROXIDE NO. IN MGM. FREE OYXGEN PER LITER GASOLINE			
	In Transparent Flasks		In Brown Flasks	
	Covered	Uncovered	Covered	Uncovered
1	0.4	0.4	0.3	Trace
3	0.7	2.7	0.6	0.5
6	1.2	15.0	0.6	1.7
12	1.2	....	0.8	4.5
15	....	4.0	....	....
19	1.2	....	1.2	7.6
23	....	73.	....	9.4
28	3.5	135.1	1.5	14.4
33	....	144.0	....	....
35	5.0	....	2.0	....

TABLE 2

Change of Peroxide Content of Cracked Gasoline on Storage

STORAGE TIME DAYS	PEROXIDE CONTENT IN MGM. FREE OXYGEN PER LITER GASOLINE			
	In Transparent Flasks		In Brown Flasks	
	Covered	Uncovered	Covered	Uncovered
Original	Trace	Trace	Trace	Trace
1	0.3	0.5	"	"
3	0.6	1.5	0.4	0.5
6	0.8	0.8	0.5	1.5
12	1.0	....	0.8	2.5
15	....	33.0	....	....
19	1.2	....	1.0	3.0
23	....	66.0	....	3.8
28	1.5	102.0	1.0	6.0
33	....	176.0	....	....
35	1.5	....	1.0	7.5

TABLE 3

Change of Peroxide Content in Blended Gasoline on Storage (Straight-Run—Cracked 1:1)

STORAGE TIME DAYS	PEROXIDE CONTENT IN MGM. FREE OXYGEN PER LITER GASOLINE			
	In Transparent Flasks		In Brown Flasks	
	Covered	Uncovered	Covered	Uncovered
Original	0.3	0.5	0.5	0.5
1	0.3	0.4	0.2	0.2
3	1.0	1.5	0.6	0.9
6	1.0	8.2	0.6	1.0
12	1.5	....	1.0	2.0
15	....	37.0	....	....
19	1.7	....	1.1	2.5
23	....	80.0	....	3.5
28	1.7	111.0	1.2	3.5
33	....	192.0	....	....
35	1.7	....	2.0	4.4

TABLE 4

Change in Tests on Storage of Straight-Run Gasoline

TESTS			Original	Test 1	Test 2	Test 3	Test 4
Peroxide No. (Mgm. O_2/liter)			Trace	68	125	144	325
Color			White	.....	White	.....	White
d (15 C.)			0.680	0.680	0.682	.....	0.679
Olefines (Percent)			33	33	33	32	34
Iodine No.			98	.....	.....	.....	.....
Aniline Point			56	.....	56	.....	58
Vapor-pressure (atm.)			0.65	0.65	0.66	0.62	0.64
B. P. Characteristic			91	.....	.....	.....	.....
E. P. (° C.)			160	.....	.....	.....	.....
Octane No.			58	49.4	48.4	48.1	37.0
Acid No.			0.002	.....	0.003	0.0045	0.017
Sap. No.			0.016	.....	.....	.....	.....
Gum Test, mgm./100 cc.			2.5	3.0	1.0	3.0	2.0
Bomb Test	At 70 °C.	Induct. Time, Min.	>240	>240	>240	>240	21.5 hrs.
		Gum Test (Mgm/100 cc.)	1.0	3.6	6.0	2.0	16
	At 100 °C	Induct. Time, Min.	105	135	75	120	90
		Gum Test (Mgm/100 cc.)	67	60	44	68	89

TABLE 5

Change in Tests on Storage of Refined Cracked Gasoline

TESTS			Original	Test 1	Test 2	Test 3	Test 4
Peroxide No. (Mgm/liter)			0.5	68	110	176	350
Color			White	.....	White	.....	White
d (15 C.)			0.717	0.718	0.721	.....	0.717
Olefines (Percent)			55.0	55.0	55.0	53.0	56.5
Iodine No.			145	.....	.....	.....	.....
Aniline Point			40.0	.....	40.0	.....	41.0
Vapor Pressure (Atm.)			0.71	0.65	0.67	0.65	0.68
B. P. Characteristic			112	.....	.....	.....	.....
E. Pt. (° C.)			196	.....	.....	.....	.....
Octane No.			68.1	61.7	58.0	57.2	45.0
Acid No.			0.004	0.007	0.003	0.008	0.017
Sap. No.			0.01	.....	.....	.....	.....
Gum Test, Mgm/100 cc.			4.0	32.0	24.0	37	78
Bomb Test	At 70 °C.	Induct. Time (Min.)	240	240	240	240	255
		Gum Test (Mgm/100 cc.)	5.4	100	180	98	1438 (21¼ hr)
	At 100°C.	Induct. Time (Min.)	70	45	30	45	30
		Gum Test (Mgm/100 cc.)	1450	1322	1154	1470	1267

TABLE 6

Change in Tests on Storage of Blended Gasoline

TESTS			Original	Test 1	Test 2	Test 3	Test 4
Peroxide No. (Mgm O_2/liter)			0.5	68.0	125	190	305
Color			White	.....	White	.....	White
d (15 °C.)			0.699	0.704	0.699	.....	0.700
Olefines (Percent)			44	45	44	44	44.5
Iodine No.			124	.....	.....	.....	.....
Aniline No.			48	.....	47.5	.....	50.5
Vapor Pressure (Atm.)			0.66	0.67	0.70	0.61	0.64
B. P. Characteristic			103	.....	.....	.....	.....
E. Pt. (°C.)			187	.....	.....	.....	.....
Octane No.			65	59	51.8	50.7	38.5
Acid No.			0.0033	0.005	0.006	0.007	0.019
Sap. No.			0.003	.....	.....	.....	.....
Gum Test, Mgm/100 cc.			1.0	17.0	24.5	24.0	38.0
Bomb Test	At 70 °C.	Induct. Time, Min.	240	240	240	240	10½ hr.
		Gum Test (Mgm/100 cc.)	5.0	27.0	60.0	79	434 (21½hr.)
	At 100°C.	Induct. Time, Min.	85.0	60.0	40.0	45.0	35
		Gum Test (Mgm/100 cc.)	770	467	641.5	820	536

TABLE 7

Storage Tests with Stablized Straight-Run Gasoline (95 Percent at 148.)

TESTS	GALV'D IRON		IRON DRUM		GALV'D IRON		IRON DRUM		GALV'D IRON		IRON DRUM		GALV'D IRON		IRON DRUM	
	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years
Addition Made	Original—No Addition				Cresol, 0.02gm/100 cc.				Power Alcohol, 11.5% Vol.				TEL, 0.5 cc/Liter			
Color	White	White	White	White	White	White	White	White	White	White	White	White	Red	Red	Red	Red
d, 15 C.	0.680	0.678	0.679	0.679	0.680	0.678	0.680	0.678	0.692	0.692	0.692	0.691	0.680	0.680	0.680	0.679
Peroxides, (Gm O_2/1000 l.)	Trace	590	Trace	760	Trace	2.7	Trace	Trace	Trace	7.6	Trace	10.0	Trace	160	Trace	460
Vapor-Press. (Atm.)	0.66	0.61	0.64	0.65	0.61	0.61	0.61	0.64	0.80	0.75	0.70	0.68	0.65	0.62	0.62	0.60
Octane No. (Research)	58.5	Bel. 41	58.5	Bel. 41	58.5	54	58.5	55.0	67.8	68.4	67.8	67.0	72.0	72.5	72.0	65.6
Addition Made	Alcohol + Cresol				TEL + Cresol				TEL + Alcohol				Alcohol, Cresol, TEL			
Color	White	White	White	White	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
d, 15 C.	0.691	0.691	0.692	0.690	0.680	0.679	0.680	0.679	0.692	0.690	0.692	0.690	0.692	0.691	0.692	0.690
Peroxides, (Gm O_2/1000 l.)	Trace	2.7	Trace	4.1	Trace	1.7	Trace	5.8	Trace	11.4	Trace	9.0	Trace	9.4	Trace	9.0
Vapor-Press. (Atm.)	0.75	0.70	0.75	0.70	0.67	0.63	0.71	0.70	0.74	0.73	0.70	0.69	0.77	0.70	0.75	0.69
Octane No. (Research)	67.8	67.0	67.8	67.7	72.0	75.4	72.0	76.9	83.4	84.9	81.3	82.4	89.3	83.2	82.8	82.4

TABLE 8

Storage Tests with Stabilized Cracked Gasoline (95 Percent at 185.)

TESTS	GALV'D IRON		IRON DRUM		GALV'D IRON		IRON DRUM		GALV'D IRON		IRON DRUM		GALV'D IRON		IRON DRUM	
	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years
Addition Made	Original—No Addition				Cresol, 0.02gm/100 cc.				Power Alcohol, 11.5% Vol.				TEL, 0.5 cc/Liter			
Color	White	White	White	White	White	White	White	White	White	White	White	White	Red	Red	Red	Red
d, 15 C.	0.776	0.721	0.718	0.724	.....	0.718	.....	0.719	.....	0.725	.....	0.727	.....	0.719	.....	0.719
Peroxides, (Gm O_2/1000 l.)	0.5	1420	0.5	990	1.0	31	0.5	17	1.0	169	1.0	123	1.0	67	0.5	990
Vapor Press. (Atm.)	0.70	0.62	0.72	0.53	.....	0.63	.....	0.63	.....	0.68	.....	0.71	.....	0.59	.....	0.67
Octane No. (Res.)	65.5	Bel. 43	65.5	Bel. 43	65.5	62.8	66.5	61.6	77.4	71.2	77.4	73.3	80.6	80.8	80.6	68.3
Addition Made	Alcohol + Cresol				TEL + Cresol				TEL + Alcohol				Alcohol, Cresol, TEL			
Color	White	White	White	White	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
d, 15 C.	.....	0.926	0.725	0.725	.....	0.722	.....	0.720	.....	0.727	.....	.....	.....	0.727	.....	0.726
Peroxides, (Gm O_2/1000 l.)	0.5	1.7	0.5	20.	1.00	38	1.0	17.0	1.0	101	0.5	.....	0.5	62.5	0.5	46
Vapor Press (Atm.)	.....	0.73	.....	0.68	.....	0.50	.....	0.58	.....	0.66	.....	.....	.....	0.72	.....	0.72
Octane No. (Res.)	77.4	73.0	77.4	72	80.6	80.5	80.6	81.	87.4	84.9	88.3	.....	89.0	83.0	88.3	86.0

TABLE 9

Storage Tests with Stabilized Blended Gasoline Mixture

TESTS	GALV'D IRON		IRON DRUM		GALV'D IRON		IRON DRUM		GALV'D IRON		IRON DRUM		GALV'D IRON		IRON DRUM	
	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years	Initial Test	After 2 Years
Addition Made	Original—No Addition				Cresol, 0.02gm/100 cc.				Power Alcohol, 11.5% Vol.				TEL, 0.5 cc/Liter			
Color	White	White	White	White	White	White	White	White	White	White	White	White	Red	Red	Red	Red
d, 15C	0.690	....	0.698	0.703	....	0.697	....	0.701	....	0.706	....	0.709	....	0.696	....	0.698
Peroxides, (Gm O_2/1000)	0.5	....	0.5	1035	0.5	3.4	trace	7.6	0.5	34.	trace	67	0.5	8.2	trace	136
Vapor Pressure (Atm.)	0.66	....	0.66	0.50	....	0.64	....	0.60	....	0.70	....	0.69	....	0.56	....	0.58
Octane No. (Res.)	63	....	63	44	63	60.2	63	58.2	72.5	71.2	72.5	71.2	77.7	79.3	77.7	76.1
Addition Made	Alcohol + Cresol				TEL + Cresol				TEL + Cresol				Alcohol, Cresol, TEL			
Color	White	White	White	White	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
d, 15C	....	0.705	....	0.708	....	0.698	....	0.697	....	0.709	....	0.710	....	0.705	....	0.707
Peroxides, (Gm O_2/1000P.)	0.5	4.1	trace	14	0.5	8.3	trace	7.0	0.5	54.0	0.5	30.5	trace	11	0.5	17
Vapor Pressure (Atm.)	....	0.73	....	0.74	....	0.64	....	0.60	....	0.75	....	0.73	....	0.72	....	0.64
Octane No. (Res.)	72.5	70.5	72.5	71.2	77.7	79.3	77.7	76.9	85.1	84.9	84.3	85.6	85	86	84.3	84

peroxide increase is at a very minimum in all cases during the storage test, and the octane number remained unchanged. In storage in unlined steel drums, however, TEL additions a definite increase in peroxide is evident with corresponding decrease in octane number; perhaps the TEL had been decomposed. This was not tested further. The mixtures behaved according to the above.

Mention should be made here that these results substantiate our remarks made under 1, even though now we note here the very high peroxide contents. The evaporation tests (dish) despite two years of storage, show no great increase over the original straight-run gasoline. The bomb test at 70° C. showed an induction-time of 240 minutes giving 3.5-3.8 mgm gnm per 100 cc. In the case of the cracked gasoline there was, of course, a marked degradation in this respect but which the addition of cresol prevented almost completely.

In conclusion it can be said that, as to peroxide-octane relationships, octane number decreases with peroxide increase very markedly, when vapor pressures of the gasolines are kept constant. Great attention was paid to maintaining constant-vapor-pressure gasolines.

3. Quantitative Relation Between Peroxide Number and Octane Number

The values given under 1, on change in octane number with peroxide value, have been quantitatively checked and re-evaluated. The results are pictured in Figure 4.

A very definite decrease is seen which amounts to 14 octane units at 200 mgm. O_2 per liter. A corresponding decrease in octane could not be established for the gasoline stored in iron drums. Again for the straight-run gasoline, contrariwise, no change in octane number resulted even at 160 mgm oxygen per liter, while the decrease was 6 units at 460 mgm.

In the case of the blended or mixed gasoline the relations are even poorer—1.5 points decrease at 136 peroxide number; in the case of the cracked gasoline larger differences became evident: an octane number of 3-4 units at 100 P.O. No., and 6 units at a P.O. No. of 170 Schildwachter shows in his contributions that the gasolines he tested gave a decrease in octane number of 2 units for 200 mgm. of oxygen per liter.

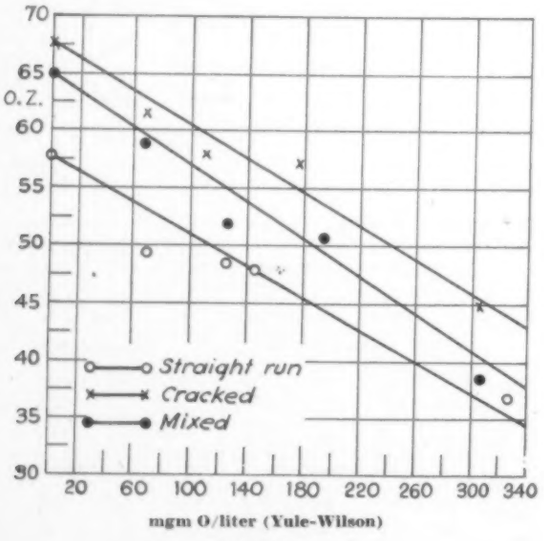

FIGURE 4
Relation between Research octane number and peroxide content.

TABLE 10
Change in Octane No. of Peroxide-Containing Gasolines with Peroxide Removal

GASOLINE TEST	Peroxide No.	Vapor Press. (Atm.)	B. P. Constant	Octane No.
Original Gasoline:				
1. Test	Trace	0.68	79	55
(a) Aged	220			49
After Peroxide Removal	9	0.65	79	53
(b) Aged	>1000	0.60	81.5	23
After Peroxide Removal	14	0.59	82	43.5
Original Gasoline:				
2. Test	Trace	0.61	80	48
(a) Aged	120			39
After Peroxide Removal	5	0.59	81	46
(b) Aged	825	0.58		27
After Peroxide Removal	17	0.56	82	43
Original Gasoline:				
3. Test	Trace	0.75	80.5	48
(a) Aged	320	0.71		39
After Peroxide Removal	8	0.66	82.0	45
(b) Aged	1170	0.70		33
After Peroxide Removal	13	0.61	81.5	42

It can therefore be established that octane decreases with peroxide increase, and depends also very much on the nature of the gasolines, as well as on the nature of and the manner in which the peroxides themselves are formed in storage. The degree of octane decrease is, of course, only partly evident from these figures which only crudely relate these two properties.

4. Change in Octane Number by Removing the Peroxides

It is of especial importance now to see if it is possible to bring gasolines which show reduced octane numbers back to their original octane number by some method for removing the peroxides. For this purpose we aged, artificially, several of the gasolines, determined peroxides and octane number, followed by the removal of peroxides by the customary washing method (using acidic ferrous sulphate solution). The results are shown in Table 10.

Using ferrous sulphate, peroxides are removed down to mere traces. To some extent, as well, there is a marked improvement in the octane number, though in no case was the original octane ever recovered by this procedure. The reason for this is partly due to the fact that when the gasoline is shaken with the aqueous chemical a portion of the very-lowest-boiling-point material is lost by evaporation. In this connection it is seen that the vapor pressure in all cases had dropped appreciably—in Test No. 3 very much—from 0.75 to 0.61. Vapor pressure is well related to the content of light hydrocarbons, butane, etc.; with respect to the content of light material to vapor pressure Test 3b shows that in order to raise the vapor-pressure from 0.61 to 0.75 an addition of between 3-4 percent butane is required, whereby the octane number increased from 42 to 46 units. Other tests show the same effects, and that in all cases the original octane number is hardly ever recovered. One would have to conclude that when appreciable quantities of peroxides form, a change in the chemical structure of the gasoline also occurs, which is not encompassed by Yule & Wilson's peroxide method (or compensated for) and which is not detected by the ordinary physical and chemical tests that are commonly employed in light-oil testing.

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Spectroscopic Analysis in the Petroleum Industry

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IN THIS discussion of spectroscopy and its application to the oil industry, the authors explain the fundamentals of the spectrum of emission and the absorption spectra, both infrared and ultraviolet. They indicate the practical application in refining of ultraviolet and infrared absorption to the analyses of hydrocarbon mixtures and stress the advantages of spectroscopic methods for rapid plant control. The Raman effect is discussed briefly, although the long exposure times militate against its use in industry. The principle of the mass spectrograph is included for completeness, since this instrument usually is classified as spectrographic apparatus, although it is strictly a mass analyzer.

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NATURE provides many examples of the splitting up of light into its various components. For example, the colors of the rainbow, the colors seen in gems and in thin films of oil on water are familiar to all, though it was not until the seventeenth century that it was demonstrated by Sir Isaac Newton that these colors are present in the original light and not in the media in which they are observed. Newton in his demonstration of this used a glass prism and a lens, an arrangement which forms the basis of all prism spectrographs. His experiment is illustrated in Figure 1.

Action of the Prism—Wavelength, Frequency, and Wave Number

Suppose that a beam of white light from a source (1) (such as a hole in a dark blind illuminated by daylight, or an ordinary electric lamp) falls on the prism (3). Then on a screen (4 to 5) a series of rainbow colors is seen arranged always in the same order, from violet at the point (4), through blue, green, yellow, and orange to red at (5). The prism has produced a "spectrum" by splitting up white light into its component parts.

The modern theory of light is a combination of the older corpuscular (or particle) and wave theories, it now being considered that light is characterized by a rapid succession of wave groups. For the purposes with which this article is concerned, however, light may be regarded as a continuous succession of waves. The most characteristic features of any system of waves are—the wavelength, λ, or distance between successive crests, and the frequency, ν, or number of waves per second.

These two characteristics are not independent, since if c is the (constant) velocity of light $c = \lambda \cdot \nu$; thus, ν is inversely proportional to λ.

Frequency may be expressed in another manner—viz., as wave number, or number of vibrations or waves per centimeter length; i.e., wave number = $1/\lambda$ (dimension: cm^{-1}). It is the frequency, wavelength, or wave number which determines, in the visible spectrum, the color sensation which the eye and brain perceive.

The Complete Spectrum

There is a much wider range of wavelength than that forming visible light, and the complete range is illustrated in Figure 2. For convenience it is usual to split up this enormous range into bands. Thus we have cosmic rays of extremely short wavelength and pass with increasing wavelength through X rays, ultraviolet rays (chemically active), visible light, infrared (heat) rays to wireless waves. These ranges merge into one another imperceptibly, but their rough limits are as indicated in Figure 2.

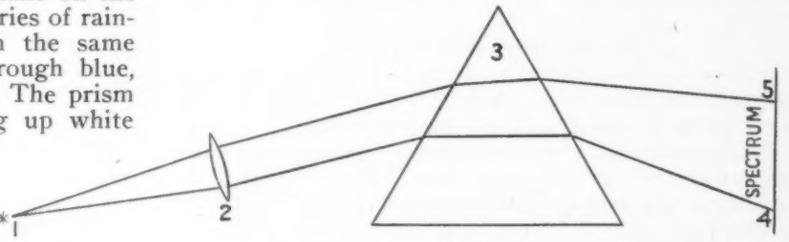
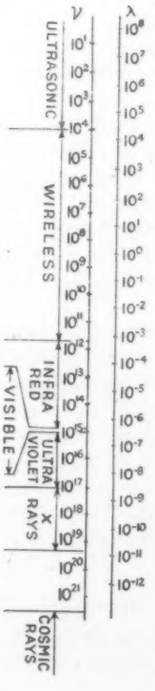


FIGURE 1
Production of spectrum by prism and lens
(1) Light source, (2) Lens, (3) Prism, (4 to 5) Spectrum.



Each of these ranges yields information of value to the scientist, but it is intended to discuss only those which are normally considered to fall within the term "spectroscopy." These ranges are ultra-violet, visible light, and infrared.

Emission Spectroscopy—Line Spectra

The means of producing wavelengths corresponding to these different ranges are all essentially similar, and consist of exciting atoms either by electric means or by flames.

For example, the ordinary electric lamp emits light when heated by an electric current, and a gas mantle when heated by a flame. In addition to the visible light produced, considerable heat is evolved; in other words, infrared radiation is produced at the same time. To produce radiation in the ultra-

FIGURE 2
The electromagnetic spectrum
(λ) Wave lengths in meters, (ν) Frequency (vibrations/sec.).

violet region, electric currents may be passed through gases at reduced pressure, electric sparks may be produced between metal electrodes by applying high voltages, or the familiar arc effect may be used.

The results produced, while broadly speaking similar in that ultraviolet, visible, or infrared radiation is generated, differ in other respects according to the mode of excitation. For example, if an ordinary electric lamp is used as the source of light in the elementary prism experiment mentioned earlier, the resulting spectrum obtained will be a continuous band of light varying gradually from violet at one end to red at the other. This type of spectrum is referred to as a continuous spectrum.

If, on the other hand, the source of light is one of the well-known neon lights used in advertising, then the resulting spectrum is found to consist of a number of colored bands separated by dark spaces.

By making the initial aperture a narrow slit, and using a lens system to focus this on the receiving screen, these colored bands will be observed as a number of colored lines and the type of spectrum is referred to as a "line spectrum." Similar line spectra are produced by sparks or arcs, and it has been found that the positions of these lines on the wavelength scale are characteristic of the materials being excited, such as the gas in the lamp or the materials of the electrodes in the spark or arc. These lines are so characteristic, in fact, that they may be used to determine the composition of the electrodes. This application of spectroscopic methods is called emission spectroscopy, but is by no means the only application.

Absorption Spectroscopy

Everyone is familiar with the somewhat peculiar appearance of colored objects when viewed by the light or mercury or sodium street lighting.

When the light emitted by a mercury lamp is analyzed by a prism, it is found that the lines are mainly in the green region of the spectrum. When the green light falls, for instance, on rosy cheeks, most of it is absorbed and the remainder reflected by white skin is, of course, greenish in color. This power of absorbing certain wavelengths is widespread. When a solution is interposed in a beam of "white" light—i.e., light containing all wavelengths—it absorbs certain wavelengths, and its resulting color is due to a combination of those wavelengths which are unabsorbed. Just as, in emission work, the wavelengths emitted are characteristic of the material of the electrodes, so in absorption the wavelengths absorbed are characteristic of the absorbing materials, though in this case it is more usual to find whole ranges of wavelength (or wavelength bands) are absorbed rather than individual lines. The missing ranges in the final spectrum are referred to as absorption bands.

It has been found that this property of absorbing radiation is not confined to the visible region of the spectrum, but extends far into the ultraviolet on one side and into the infrared on the other. Thus, materials which to the eye appear colorless, show great differences when examined by ultraviolet or infrared radiation. It is these two regions of the spectrum which have found the greatest application in the petroleum industry, where most of the materials are colorless in the visible region.

Origin of Emission and Absorption Spectra

We must now consider the causes of these emission and absorption spectra. It was stated earlier that light had a dual nature, wave and corpuscular, and that a beam of light could be regarded as a rapid succession of packets of waves or "quanta." With each of these quanta there is associated a definite amount of energy related to the frequency of vibration of the waves in the quantum. Expressed mathematically, the relationship is E (energy in ergs) $= h\nu$, where $h =$ a constant, known as Planck's constant and ν frequency in vibration per second.

From this it is seen that the energy in a quantum is not constant but varies directly with the frequency, or inversely with the wavelength (frequency $\propto 1/$wavelength or $\nu \propto 1/\lambda$.

This theory was applied by Bohr to the explanation of line emission spectra on the assumption that the electrons round the atomic nucleus rotated in definite orbits. By absorbing energy, an electron could move from one orbit to another, and in returning to its original orbit could re-emit this energy. Only certain orbits at definite distances from the nucleus could be occupied by electrons, the energy differences between electrons in these orbits being fixed and made up of integral numbers of quanta. It was impossible for an electron to absorb a small amount of energy and move part of the way between two orbits. It had to absorb at least one quantum. Similarly, in the reverse direction it had to emit at least one quantum. With this quantum there is associated a frequency obtained from the Planck relationship, the frequency (or its associated wavelengths) appearing as a definite line when observed with a spectroscope.

The problem becomes more complicated when we pass from atoms to molecules. If a weight is hung on a spring in a building which is subject to periodic vibrations, when one of the vibration frequencies coincides with the natural frequency of the weight/spring system the weight will start to oscillate and in doing so will absorb energy from the vibrations of the building. Something analogous happens in the interaction between radiant energy and molecules. If we assume that a diatomic molecule consists of two solid spheres joined by a spring, then the system will have a natural frequency dependent on the masses involved and on the strength of the spring linkage. The energy of this system can be changed by increasing the amplitude of the vibrations, but, as in the case of the atoms discussed earlier, the energy of the system cannot change continuously but must proceed in steps. It is when the difference in energy between two of these steps coincides with the energy (quantum) of the incident vibration that the molecule absorbs energy and starts to vibrate. The energy absorbed will give rise to a "dark" absorption band in the spectrum of the absorbing material.

Another method exists by which the energy of the ball-spring may change, and that is by causing the system to rotate about some fixed set of axes. In addition to having these two separate methods of changing the energy it is possible to have a combination of both.

To summarize, there are three methods by which the energy of a molecule may change: by electronic changes within the atoms, by vibrations of the atoms relative to one another, and by rotation of the molecule as a whole. The energy required for each of these methods of energy change diminishes in the order given—i.e., a much smaller quantum is required to cause a change in molecular rotation than to cause a change in the electronic state of the molecule. The frequencies associated with these quanta will there-

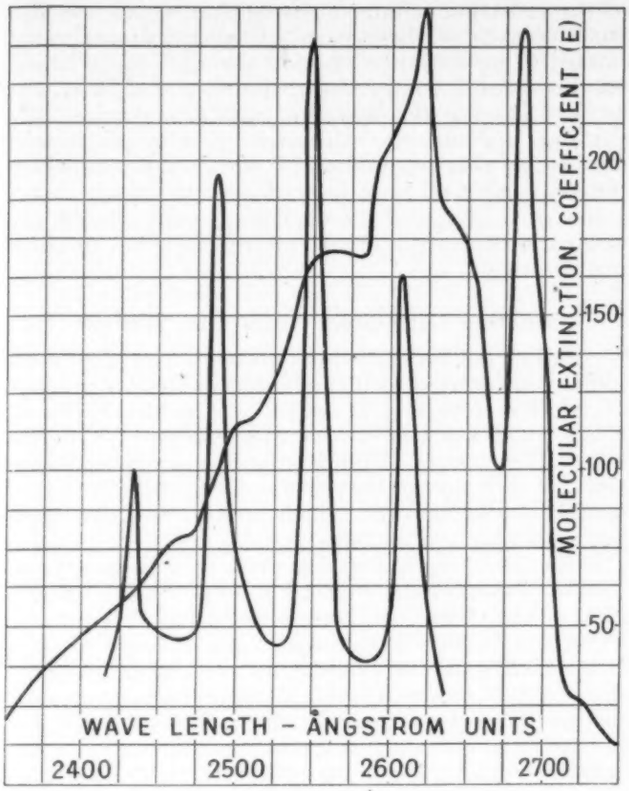


FIGURE 3
Uutraviolet absorption of spectra of toluene and benzene

fore be very high for electronic changes and low for rotational changes, vibrational changes occurring in a midway position on the frequency scale. These frequencies correspond roughly to the ultraviolet and infrared regions of the spectrum.

Strictly speaking, a series of individual lines should be observed by the spectroscope, and in many cases this is indeed what is observed. Often, however, these lines are so close together, owing to the small size of quanta required to cause changes in rotational energy, that merely the envelope of a group of lines is detected, the result being an absorption band.

Absorption by Hydrocarbons

It has long been known that all hydrocarbons absorb radiant energy in particular regions over a very wide range of the spectrum, the particular region being related to the type of molecule. For example, aromatic compounds absorb in the near ultraviolet (wavelength range 2,500-3,000 Ångströms, (1Å = 10^{-8} cm), but the saturated paraffins and naphthenes do not absorb in this range. All hydrocarbons, however, absorb in the infrared and in the far ultraviolet (below 2000 Å).

The experimental technique for the far ultraviolet is, however, extremely difficult, owing largely to the lack of suitable sources of the radiation and to the fact that the whole apparatus must be evacuated as air absorbs strongly in this region. Thus it is the long wave ultraviolet and the infrared regions of the spectrum which have found practical application in the petroleum industry.

It will be clear from the preceding explanation that a firm basis exists for at least qualitative identification of elements (atoms) or compounds (molecules) in emission or absorption spectroscopy; and the methods used will now be considered in greater detail.

Ultraviolet Absorption Methods

It has been explained that the spectra appearing in the near ultraviolet are due to changes in the electronic configuration of molecules. The electronic changes observed in absorption spectra are connected mostly with the outer electrons—that is, those electrons which are chiefly responsible for the linkages between atoms. The bands observed, therefore, are connected chiefly with the types of chemical bonds, and are only affected in a secondary manner by the rest of the molecule. For example, aromatic compounds show a series of absorption bands in the region 2500-2800 Å. Side chains on the aromatic necleus have practically no effect on the range in which absorption occurs, but cause comparatively minor differences in the arrangement of the bands within this region. As an instance of this, the absorption spectra of benzene and toluene are shown in Figure 3. The differences between these two curves are small, but are sufficient to permit identification.

Identification, however, is not the main objective in industry. Quantitative determination is required, and some consideration will now be paid to this problem.

Two of the fundamental laws of the absorption of radiant energy (Beer and Lambert's Laws) combine to yield the conclusion that the amount of radiation absorbed by each successive layer of absorbing material is a definite fraction of the radiation incident on each layer, and is also proportional to the number of absorbing molecules in the radiation path.

$$E = (1/ct).\ \log\ (I_0/I) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where

c = concentration of absorbing material (g.mol./litre)
t = total thickness of absorbing layer (cm.)
I_0 = intensity of incident radiation
I = intensity of transmitted radiation
E = molecular extinction coefficient, which is a constant for a given compound at a given wavelength.

If the thickness of the absorbing layer is 1 cm., and the concentration of absorbing material 1 g. mol. per litre, E becomes log (I_0/I), which is usually shortened to d, and called the optical density.

Rearranging the expression given above to the more convenient form $d = Ect$, it is clear that since E and t are constants (at any one wavelength) then the optical density is directly proportional to the concentration. In the case of aromatics it has been found that this relationship holds over wide ranges of concentration and thickness of absorbing layer.

The analytical procedure is, therefore, as follows.

First, the molecular extinction coefficient E for the absorbing substance must be determined at a given wavelength. This is done by using a known concentration of the material in a non-absorbing solvent, in an absorption cell of known thickness. Next, the radiation transmitted by a layer of solution of known thickness containing the absorbing material in unknown concentration, at the same wavelength, is photographed—i.e., the optical density at this wavelength is determined. For this purpose a Spekker photometer (described below) is used.

Thus, c becomes the only unknown in equation (1) and it can, therefore, be calculated.

In a mixture of absorbing substances the optical density observed at any wavelength is the sum of

the optical densities of the components at that wavelength. If, therefore, a solution is taken containing two absorbing components and the resulting optical density is measured at two wavelengths, two simultaneous equations are obtained:

$$d_1 \text{ (obs.)} = t(E_1c_1 + E_2c_2)$$
$$d_1' \text{ (obs.)} = t(E_1'c_1 + E_2'c_2)$$

where E_1 and E_2 are the molecular extinction coefficients of the two absorbing materials at one wavelength and E_1' and E_2' are the values at the second wavelength. These two equations allow the determination of c_1 and c_2, the concentrations of the two absorbing components in g. mols/litre.

Ultraviolet Apparatus

A diagrammatic representation of the apparatus used is shown in Figure 4. It comprises two main items, the Spekker photometer and the spectograph. The Spekker photometer is used for the quantitative determination of the intensity of absorption and the spectrograph is used to separate the various wavelengths from one another, and for recording the intensities on a photographic plate.

The source of ultraviolet radiation used is an electric spark operated at 15,000 volts between tungsten - steel electrodes. The radiation from the spark (1) is divided into two beams by the two quartz rhombs (2,3). The upper beam passes through an aperture of fixed area (4), and then through a cell containing the solution (5) under examination, while the lower beam passes through an exactly similar cell containing the pure solvent (6). A variable aperture (7) is placed in the path of the lower beam.

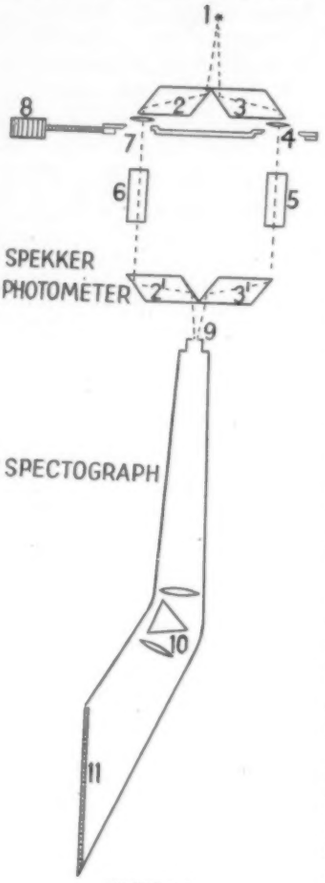


FIGURE 4

Optical lay-out of Hilger medium quartz spectrograph and Spekker photometer.

(1) Spark, (2), (2^1), (3^1), quartz rhombs, (4) Aperture and fixed area, (5) Solution cell, (6) Solvent cell, (7) Aperture of variable area, (8) Drum, (9) Slit of spectograph, (10) Quartz prism, (11) Photographic plate for recording spectrum.

The two beams are then brought to a focus close together on the slit of the spectrograph (9).

A series of photographs is taken with different ratios of the variable to the fixed apertures. These photographs appear on the photographic plate (11) as pairs of spectra, the members of each pair being separated by a very narrow gap. The blackening of a photographic plate is proportional to the intensity of the radiation falling on it, so that where the two parts of each of these pairs of spectra are of equal intensity the radiation coming through the solution has been cut down by absorption to the same extent as that passing through the variable aperture. The variable aperture is calibrated directly in optical density, so that by noting the wavelengths at which the two parts of each pair of spectra match, for a series of readings of the variable aperture scale, the absorption spectrum of any mixture may be obtained quantitatively.

Another Ultraviolet Absorption Method

Another method by which absorption in the ultraviolet can be used to identify and analyze a mixture of two hydrocarbons is well illustrated in Figure 5. It shows 10 ultraviolet spectra placed one above the other. The source of light in this case produces a continuous spectrum in the ultraviolet (unlike the spark used with the Spekker, which produces a large number of closely spaced lines).

If no absorbing material is present, a positive print of the photograph obtained would have shown a clear white band stretching from left to right of Figure 5. If now a cell with quartz windows (for transparency to ultraviolet) and containing a solution of the aromatic hydrocarbon, meta-xylene, is placed between the source and the spectrograph, the radiation is absorbed at certain wavelengths, these regions showing black areas in Figure 5. Similarly, if para-xylene is used instead of meta-xylene and another photograph is taken, we get the bottom line of the figure. Looking at the top and bottom lines, we see that the absorption bands at A and E can be used to distinguish para-xylene and that at B to distinguish meta-xylene. The other two bands at C and D give us no help, since they appear in both spectra.

If mixtures are made containing varying proportions of the two hydrocarbons, starting with 20 percent of meta-xylene and 80 percent of para-xylene, and the proportions altered in a series of steps until 80 percent of meta-xylene and 20 percent of para-xylene are reached, by photographing the spectrum for each mixture eight intermediate spectra shown in Figure 5 are obtained. The spectrum for the 65 percent of meta-xylene and 35 percent para-xylene mixture shows that all five of the bands are clearly present. Looking down the figure from top to bottom, it is seen that the amount of absorption at B is decreasing as the percentage of meta-xylene falls and the amount of absorption at E and A is increasing.

A photograph of a mixture of the two hydrocarbons of unknown composition should allow us to tell from its appearance how much of each component is present. In this way the amount of meta-

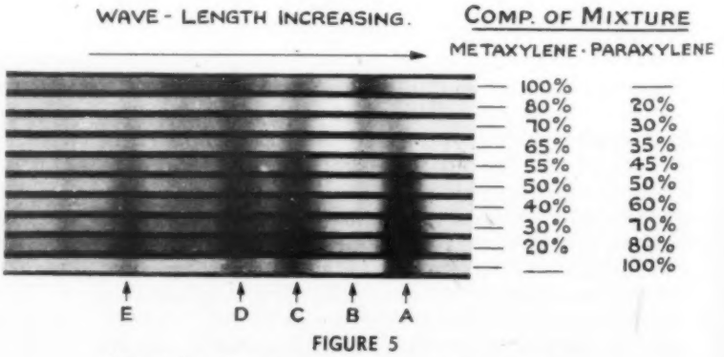


FIGURE 5

Ultraviolet absorption of spectra of toluene and benzene

xylene in the mixture can be judged to the nearest 5 percent, but a still more accurate figure can be found if careful measurements of the relative blackening at B as compared with that at A and E are made. Such measurements can be made using a microphotometer.

Using the methods described, the spectrograph is now engaged in routine analyses of aromatic hydrocarbons and conjugated dienes.

Infrared Methods

The infrared region of the spectrum is usually understood to cover the range 0.7-150μ (where $1\mu = 10{,}000$ Å $= 10^{-3}$ mm). This is an extremely wide range of wavelengths, and the experimental difficulties of observing a large part of it preclude its use in industrial work. The shorter wave portion as far as 28μ, however, can be observed fairly readily, and it is with this range that we are particularly concerned.

The absorption bands observed in this region are due to the vibrations of the atomic nuclei, with respect to one another and to the rotation of the molecule as a whole. In a molecule made up of n atoms there are $3n$ possible modes of vibration, rotation, and translation. Of this number, 6 are taken up by rotation and translation of the molecule as a whole about some space-fixed system of coordinates, leaving $3n$-6 possible methods of inter-atomic vibration. Not all of these are "active" in the infrared. Only those appear which involve a change in the electric moment of the molecule. Whether there is a change in the electric moment or not is dependent on the symmetry of the molecule. For example, the carbon dioxide molecule is known to be linear, with the carbon atom in the center and the oxygen atoms equally spaced on either side. There are three possible modes of vibration as shown in Figure 6.

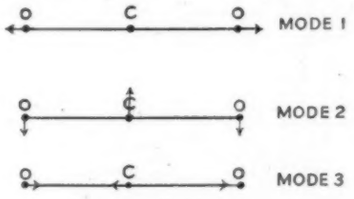


FIGURE 6

Vibration of the carbon-dioxide molecule. Mode 1: Symmetrical (inactive in infrared, active in Raman); Mode 2: Bending (active in infrared, inactive in Raman); Mode 3: Asymmetrical (active in infrared, inactive in Raman).

Of these modes, 2 and 3 involve a change in the electric moment and these appear as absorption bands in the infrared, but mode 1 being perfectly symmetrical does not appear.

The masses of the atoms and the forces which bind them together regulate the position of the bands in the spectrum.

From what has been said about the appearance and positions of infrared absorption, it is clear that no two hydrocarbons should have the same absorption spectrum (with the possible exception of optical isomers), and this should provide a very good method of "fingerprinting" the various hydrocarbons. However, apart from these fundamental bands—that is, bands caused by the absorption of a single quantum causing the vibration in question to rise to the next energy level—other bands appear corresponding to higher energy levels. Such bands correspond to frequencies of vibration twice or three times that of the original fundamental band. In addition to these overtone bands other bands appear owing to the combination of two fundamental frequencies. It can be seen, therefore, that, with increasing number of atoms in the molecule, the absorption spectrum produced may become very complicated, especially in molecules with low symmetry, and the chance of interference between the absorption bands of the components of a mixture increases greatly. However, the field of usefulness has not as yet been covered even for hydrocarbons, and the limit is not yet in sight.

Infrared Apparatus

In principle the apparatus used is similar to that described for the ultraviolet region. The main differences lie in the substitution of a rock salt prism in place of the quartz prism, the use of focusing mirrors instead of lenses, and a thermopile for detection in place of the photographic plate. These changes are necessary owing to the opacity to infrared radiation of glass and quartz beyond short wavelengths, and to the fact that a photographic plate is not affected by infrared radiation of wavelengths greater than about 12,000 Å. A schematic arrangement is shown in Figure 7 of a typical infrared instrument.

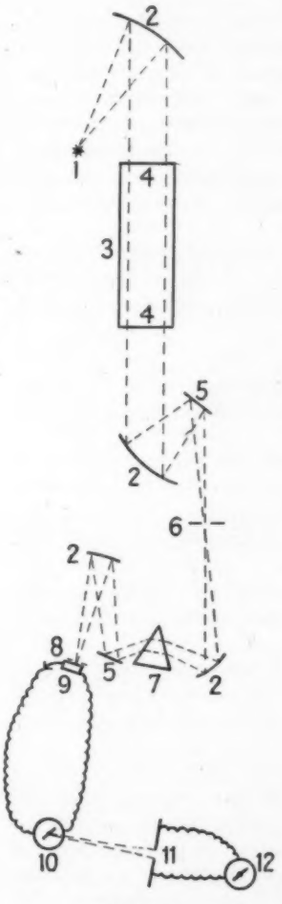


FIGURE 7

Typical infrared spectrometer

1, Light source; 2, Concave mirrors; 3, Absorption cell; 4, Rock salt endplates of 3; 5, Plane mirrors; 6, Slit of spectrometer; 7, Rock salt prism; 8, Exit slit of spectrometer; 9, Thermopile (measurement of energy transmitted); 10, Primary galvanometer; 11, Divided photo-cell amplifier; 12, Secondary galvanometer.

From what has been stated earlier in this paper, all hydrocarbons will show absorption in the infrared. This may lead to an embarrassingly large number of possible components in a mixture to a maximum of about eight. However, this is not usually a difficult procedure and normally involves only straight-forward distillation by well-known standard procedures. Consequently, infrared spectroscopic analysis has found many applications in the petroleum industry.

Applications

As an example of the general procedure the analysis of mixtures of normal and isobutane will be discussed.

The absorption spectra of the two hydrocarbons are shown superimposed in Figure 8. From this it is at once clear that the best wavelengths at which to measure the absorption are 8:58μ and 10:34μ, where the main absorption is due to isobutane and normal butane respectively. Again the assumptions are made that the optical density

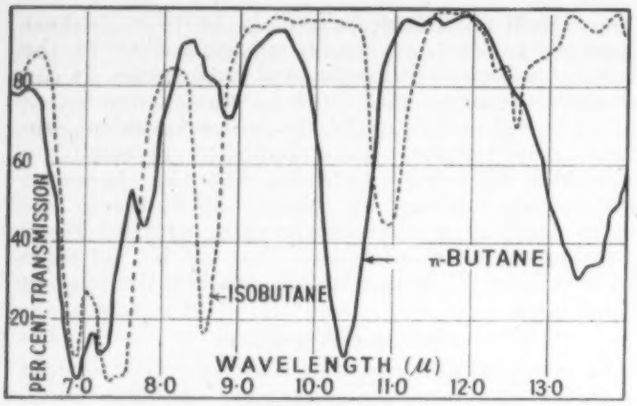


FIGURE 8
Infrared absorption spectra

is proportional to the concentration (pressure in the case of gaseous samples) and that the optical density of the mixture is the sum of the optical densities due to the components. As before, this leads to two equations which on solution should give the required analysis.

Unfortunately, there are several factors, some of which are only imperfectly understood at present, which invalidate the assumption of a linear relationship between optical density and concentration, so that the result obtained by straightforward solution of equations must be regarded as an approximation to the true result. By the application of factors derived from empirical calibration curves, however, the true result is obtained.

This is an extremely simple example and does not demonstrate the real usefulness of the method, but the treatment of more complicated mixtures is beyond the scope of this article.

It may be stated, however, that in many cases some mathematical simplification is possible of what would otherwise be a complicated process of solving a large number of simultaneous equations derived from multi-component mixtures. In other cases it is possible to employ electrical or mechanical devices either to carry out the computation or to produce the complete analysis, either by synthesising from the component absorption spectra a replica of the experimentally determined absorption curve of the mixture or by breaking down this curve into its component parts.

The importance of such aids to analysis, particularly in industrial plant control work, where speed in analysis may be so vital, is likely to increase very greatly.

The Raman method of analysis differs from either the ultraviolet or infrared method in being observed by emission and not by absorption. It is similar to fluorescence, but differs in that it is independent of the wavelength of the incident light. It is instantaneous and, in comparison, of feeble intensity.

It may be recalled that fluorescence occurs in some materials which absorb relatively short wavelength radiation and emit radiation of longer wavelength so long as the exciting stimulus is maintained.

The Raman effect may be explained briefly as follows. When a quantum of energy collides with a molecule part of its energy may be redistributed over the internal degrees of freedom of the molecule. The oscillating electro-magnetic forces in the incident light induce oscillating dipole moments in the molecule, and these re-radiate energy of the same frequency, but in different directions to that of the incident light. Superimposed on this frequency is the frequency of vibration of the atoms within the molecules, and the result of the interaction between these two frequencies can be regarded as being made up of three frequencies V, $V+V_0$ and $V-V_0$, where V = frequency of incident light and V_0 is a natural frequency of vibration of the atoms within the molecule.

If, therefore, a solution is irradiated with monochromatic light and the scattered light is passed into a spectrograph, the resulting photograph shows a line corresponding to the wavelength of the original ray accompanied by weaker lines. These are the Raman lines. It has been found in many cases that the differences between the original frequency and those of the various Raman lines are the same as frequencies occurring in the infrared absorption spectrum of the same molecule. There is not complete coincidence in most cases, some Raman lines having no counterpart in the infrared, and vice versa. This is due to the different laws governing the activity of the frequencies in the two phenomena, the Raman-effect lines appearing not when there is a change in the electric moment of the molecule, but when there is a change in the "polarisability" (that is, the probability of an electron moving from one atom to another).

In the case of a symmetrical molecule (CO_2 for

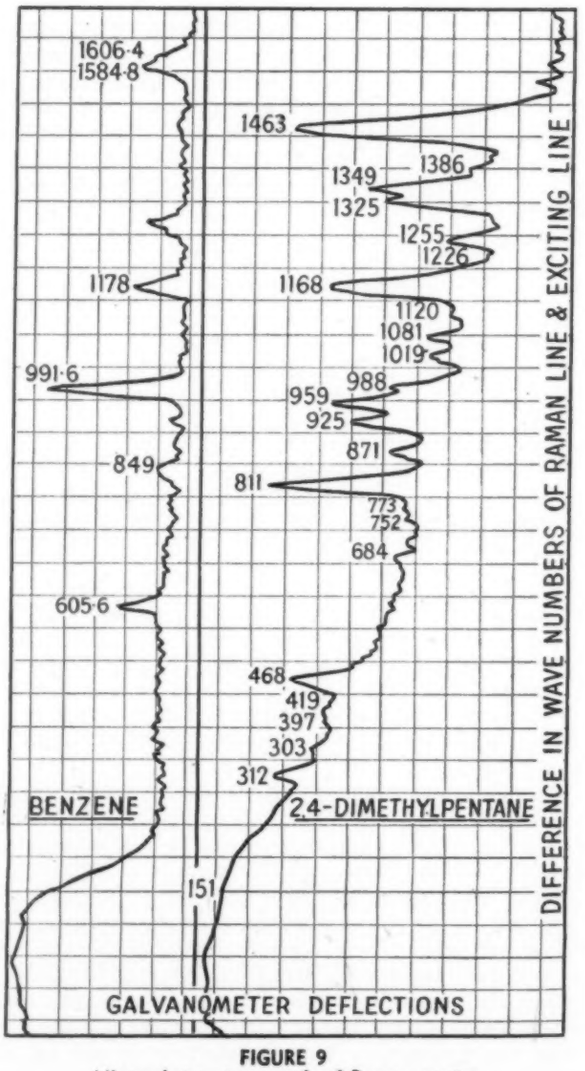


FIGURE 9
Microaphotometer records of Raman spectra

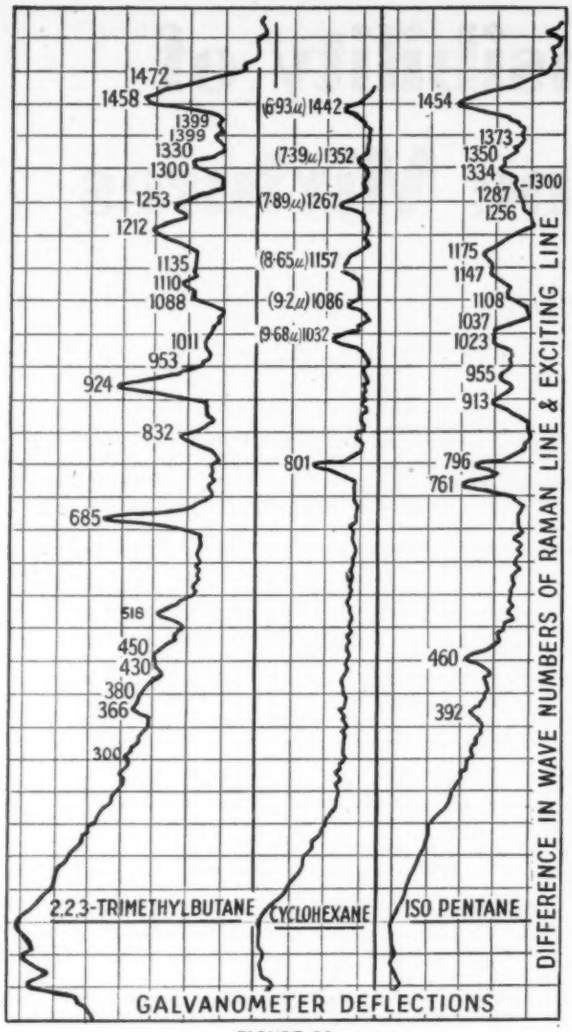


FIGURE 10
Microphotometer records of Raman spectra

example) in a totally symmetrical vibration (mode 1) the polarisability is not the same in the two extreme positions, and this line, therefore, appears in the Raman effect. In general, it can be said that the greater the symmetry of the molecule the fewer are the coincidences between Raman and infrared. In this way the two phenomena may be said to be complementary.

The other factors governing the positions of the Raman lines are the same as for the infrared, and hence we have in this effect another method of identifying hydrocarbons.

The Raman effect has the advantage that the apparatus required is relatively simple and robust. It consists of a sealed glass tube irradiated from the side by mercury arcs, the light scattered along the axis of the tube being passed into the spectrograph and photographed.

The Raman effect probably has applications as wide as those of the infrared, but it suffers from the great defect at present of being extremely time-consuming, the exposures necessary running into some hours in favorable cases. For this reason, it has not been applied to any great extent in quantitative analysis. Typical records obtained by using a microphotometer on the photographic plates are shown in Figures 9 and 10.

The mass spectrograph is a method of hydrocarbon analysis which has recently come into prominence, but strictly speaking the method is not spectrographic at all. However, a brief outline of the method is given, since it is associated with spectrographic methods of analysis.

In the mass spectrograph, molecules[1] are split into charged fragments (ionised) by bombardment with electrons.[2] These charged particles[3] are accelerated by an electric field,[4] and in passing through a magnetic field[5] follow curved paths[6] whose radii are proportional to the masses of the particles. If the conditions within the apparatus are carefully standardized, then the relative abundance of particles of different masses are characteristic of the original molecule. By plotting the abundance against the masses for a given molecule a result is obtained which resembles a spectrum; hence the name applied to this method. Once these "spectra" have been obtained, then by using methods of computation analogous to those described earlier for ultraviolet and infrared spectra, analysis of mixtures is possible.

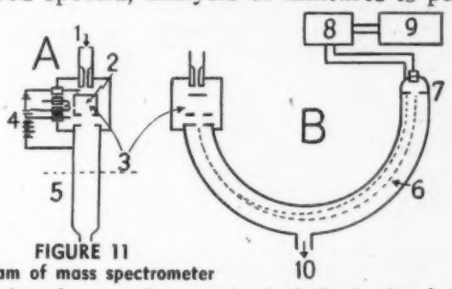


FIGURE 11
Diagram of mass spectrometer

1, Inlet of gas to be examined; 2, Ionisation by bombardment with electrons; 3, Accelerating field; 4, Batteries producing electric field; 5, Magnetic field; 6, Curved paths followed by charged particles; 7, Slit of receiver; 8, Amplifier; 9, Mass spectrum recorder; 10, Vacuum pump (A and B are sections at right angles to each other).

Figure 11 shows the principle of the mass spectrograph, including both the ionisation and the ion analysis on a mass basis.

Conclusion

The method and apparatus to be used naturally depend on the problem being investigated. For example, if metallic elements are sought, then emission spectra using quartz prisms and photographic plates are indicated. If the analysis desired is for aromatic hydrocarbons only present in mixtures of paraffins and aromatics, then the ultraviolet absorption method is used; but if a complete analysis for paraflins, naphthenes, and aromatics is desired, then a combination of both ultraviolet and infrared methods should be used. The mass spectrograph performs a similar function, and in addition will allow the determination of oxygen, nitrogen, and hydrogen which do not show up in either ultraviolet or infrared methods. As a quantitative analytical method, the Raman effect in its present stage of development may be discounted by reason of the time required to obtain a record. The importance of the time factor in plant control has been stressed.

From what has been said, it is clear that various branches of spectroscopy which until recently have been confined to the research laboratories of universities, have now been developed to the stage of direct industrial application. The information obtained by their use has facilitated the solution of problems which would prove most intractable by any other method, and a much closer control may now be maintained on industrial processes than has hitherto been possible.

Super-Expansibility of Methane-Ethane Mixtures

W. O. CLINEDINST
National Tube Company, Pittsburgh

MOST of the formulae commonly used for determining gas flow disregard super-expansibility. One of the most widely used equations is Weymouth's, which is obtained by substituting Weymouth's friction factor[1] based on pipe diameter, equation (1), into the general expression for ideal gas flow,[2] equation (2). The resulting formula[2] is shown in equation (3).

$$f = \frac{0.032}{d^{1/3}} \quad (1)$$

$$Q_{day} = 77.554 \frac{To}{Po} \sqrt{\frac{(P_1^2 - P_2^2)d^5}{fGTL}} \quad (2)$$

$$Q_{day} = 433.484 \frac{To}{Po} \sqrt{\frac{(P_1^2 - P_2^2)d^{16/3}}{GTL}} \quad (3)$$

where d = inside diameter of pipe in inches
f = coefficient of friction of the gas in the pipe. Sometimes the coefficient of friction is expressed as a value of ¼ of that used here with the constant of the general flow equation modified accordingly.
G = specific gravity of the gas referred to air
L = length of line in miles
Po = standard atmospheric pressure in psia
P_1 = entrance pressure in psia
P_2 = exit pressure in psia
Q_{day} = capacity in cu. ft. per day at standard conditions
To = standard temperature in °F. absolute
T = temperature of the flowing gas in °F. absolute

The general flow equation (2) for ideal gas is obtained by integrating the differential equation (4) of the gas pressure gradient,[3] using the ideal gas laws defined by equation (5).

$$\frac{d(p + \gamma h)}{dx} = -\frac{f}{D}\frac{\gamma v^2}{2g} \quad (4)$$

$$PV = NR'T \quad (5)$$

where g = acceleration due to gravity in ft./sec. per second
h = elevation variation in feet
p = gas pressure in lb./sq. ft absolute
x = length along line in feet
v = velocity of gas in the line in ft./sec.
D = inside diameter of pipe in feet
N = number of lb. moles of gas = weight of gas in lb. / molecular weight
P = pressure in psia
R' = universal gas constant = 10.71 for cut. ft., psi
T = temperature in °F. absolute = 460 + temperature F.
V = volume in cu. ft.
γ = weight density of gas in lb./cu. ft.

Affects Compressors, Flow

It is well known that natural gas, which is largely mixtures of methane and ethane, expands and compresses more readily than is indicated by the ideal gas laws. This phenomenon may be referred to as super-expansibility or super-compressibility, as the case may be. Both are of importance to the design of gas lines. Super-compressibility affects the design of compressors for field and booster stations, while super-expansibility affects the flow of gas through the pipe. Extensive studies of these deviations from ideal gas laws have been made,[4,5] and it has been found that the deviations can be approximated by a compressibility factor Z, or its reciprocal, an expansibility factor Y, introduced into equa-

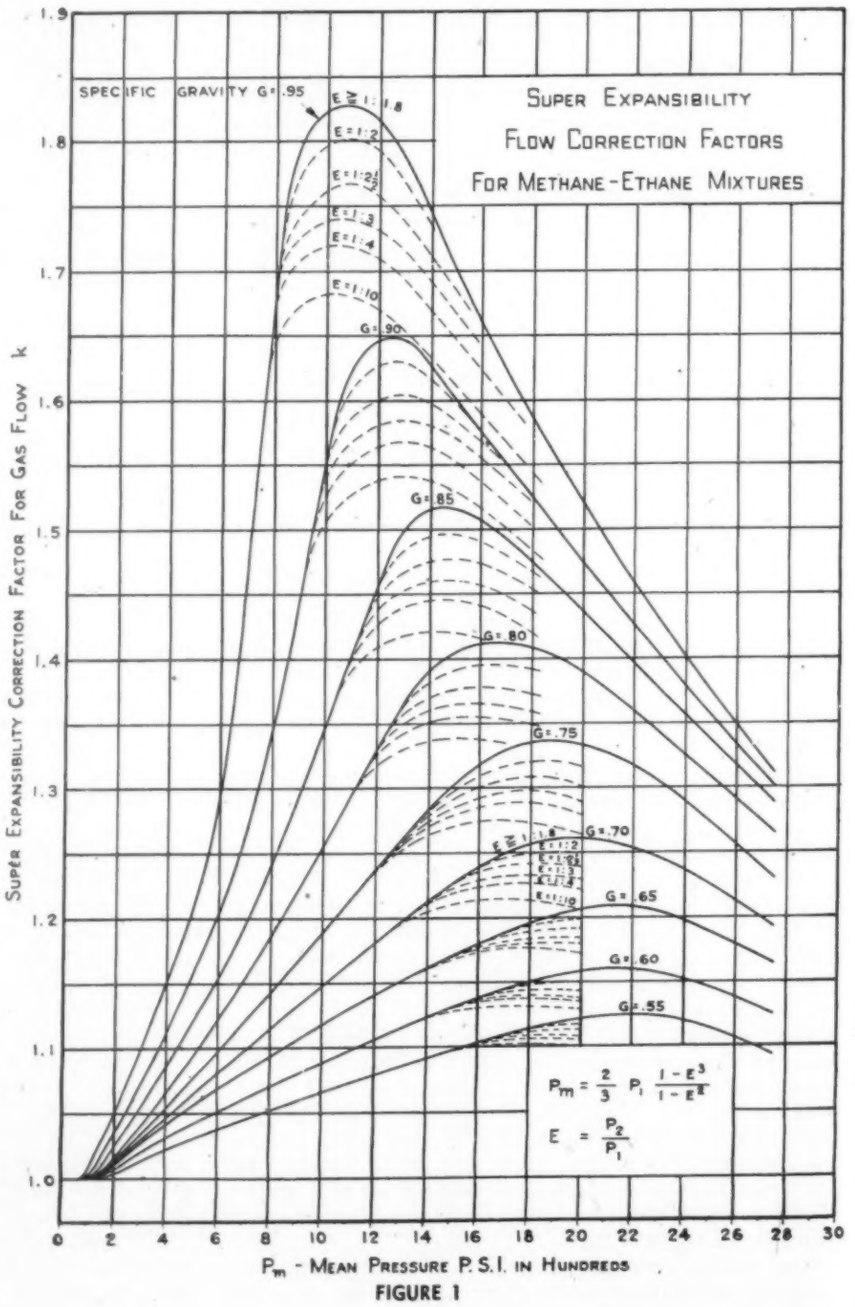


FIGURE 1

tion (5) representing the ideal gas laws, resulting equation (6).

$$PV = ZNR'T = \frac{NR'T}{Y} \qquad (6)$$

where Z = compressibility factor

Y = expansibility factor = $\frac{1}{Z}$

General Flow Equation

A flow equation taking into consideration the effect of super-expansibility has been obtained by the writer[1] by integrating the pressure gradient differential equation (4), using equation (6) rather than equation (5) to represent the gas laws. The result is the general flow equation (7) following:

$$Q_{day} = 109.6622 \frac{To}{YoPo} \sqrt{\frac{d^5 \int_{P_2}^{P_1} PYdp}{fGTL}} \qquad (7)$$

where Yo = expansibility factor at standard atmospheric pressure and temperature; which is approximately unity and may be eliminated from the equation.

Curves of the integral appearing in equation (7) have been prepared by the author[1] by means of numerical integration. These are expressed in terms of the critical pressure and temperature for general application to gas. While the integral curves are not difficult to use, considerable effort can be saved in the case of methane-ethane mixtures commonly encountered in natural gas by correction factors applied to the usual ideal gas flow equations, such as Weymouth's. Dividing equation (7) by equation (2), equation (8) is obtained representing the multiplying correction factor to be applied to ideal gas flow equations:

$$k = \sqrt{\frac{2 \int_{P_2}^{P_1} PYdp}{P_1^2 - P_2^2}} \qquad (8)$$

where k = super-expansibility flow correction factor.

From equation (8) and the pressure integral curves referred to, curves of the super-expansibility correction factor k for methane-ethane mixtures for various specific gravities at 60° F. have been calculated and are shown in Figure 1. These curves have been plotted against the mean pressure in the line based on the ideal gas flow pressure gradient shown in equation (9):

$$Pm = \frac{2}{3} P_1 \frac{1 - E^3}{1 - E^2} \qquad (9)$$

where Pm = mean line pressure based on ideal gas law pressure gradient in psia

E = expansion ratio during flow = $\frac{P_2}{P_1}$

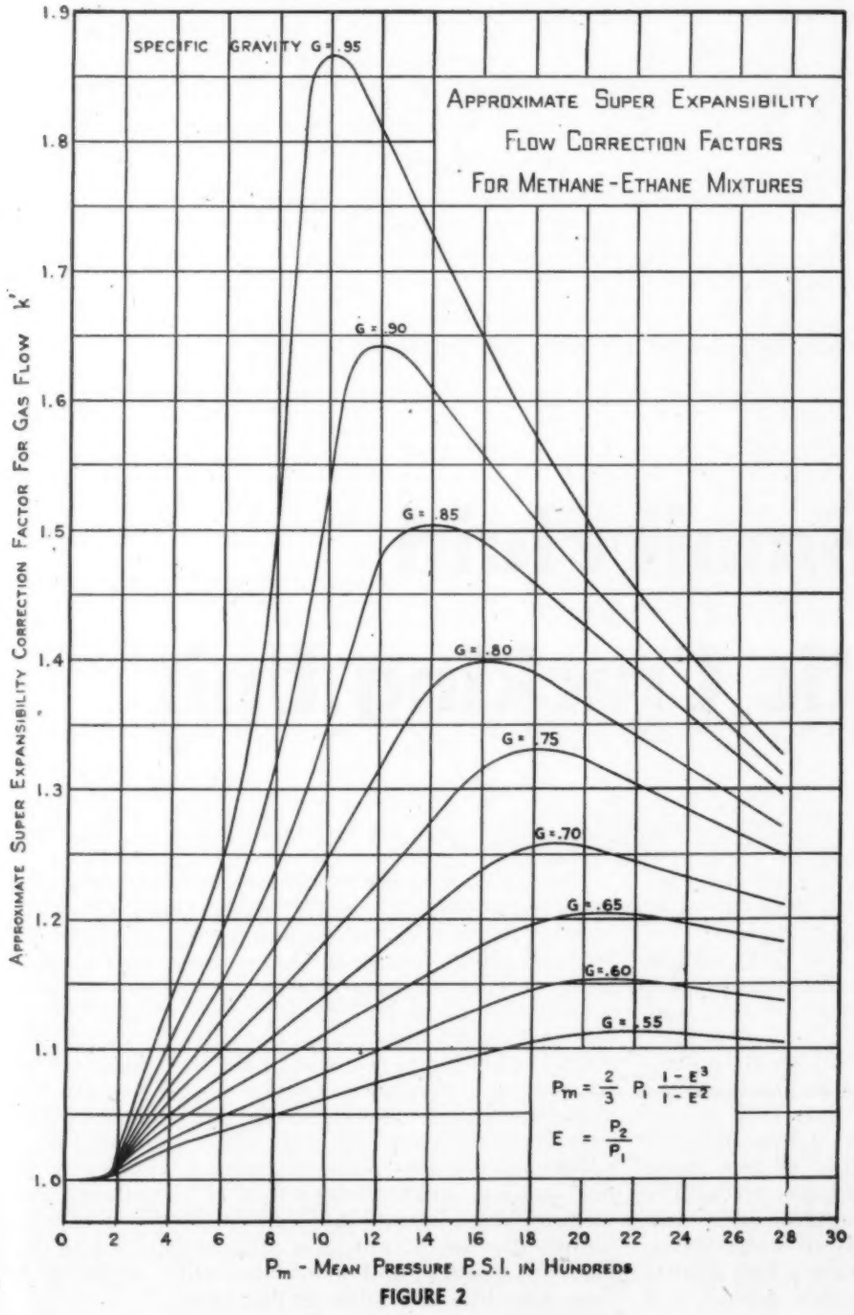


FIGURE 2

The correction factor k of Figure 1 can be used as a multiplying factor to correct ideal gas flow formulae for super-expansibility of methane-ethane mixtures.

Examining equation (8), it is seen that the integral can be evaluated approximately by using a constant value of Y corresponding to mean line pressure Pm determined by equation (9). Such approximate interpretation results in equation (10):

$$k' = \sqrt{Ym} \qquad (10)$$

where k' = appropriate super-expansibility flow correction factor

Ym = expansibility factor corresponding to mean pressure in line

The curves of Figure 2 show the approximate correction factor obtained by means of equation (10) for gas flowing at a temperature of 60° F.

Comparing the super-expansibility flow factor of Figure 1 with the approximate ones of Figure 2, it is seen that the approximate factors are somewhat higher. Also, it is to be observed that for certain pressure ranges the factors of Figure 1 are affected by expansion ratio, whereas the approximate factors of Figure 2 are not.

Typical Conditions

Consider the magnitude of the super-expansibility effect on a typical set of flow conditions. Assume a natural gas composed largely of methane and ethane, having a specific gravity of .65, with a working pressure of 1000 psi absolute, and expansion rates of 1:2.

Determining Pm from equation (9):

$$Pm = \frac{2}{3}(1000) \frac{1 - \left(\frac{1}{2}\right)^3}{1 - \left(\frac{1}{2}\right)^2} = 777.8$$

From Figure 1 for the specific gravity of .65 and mean line pressure of 777.8 psi absolute, the super-expansibility correction factor is 1.09. The capacity of the line is then obtained by multiplying the capacity for ideal gas by Weymouth's or other suitable equation by this factor.

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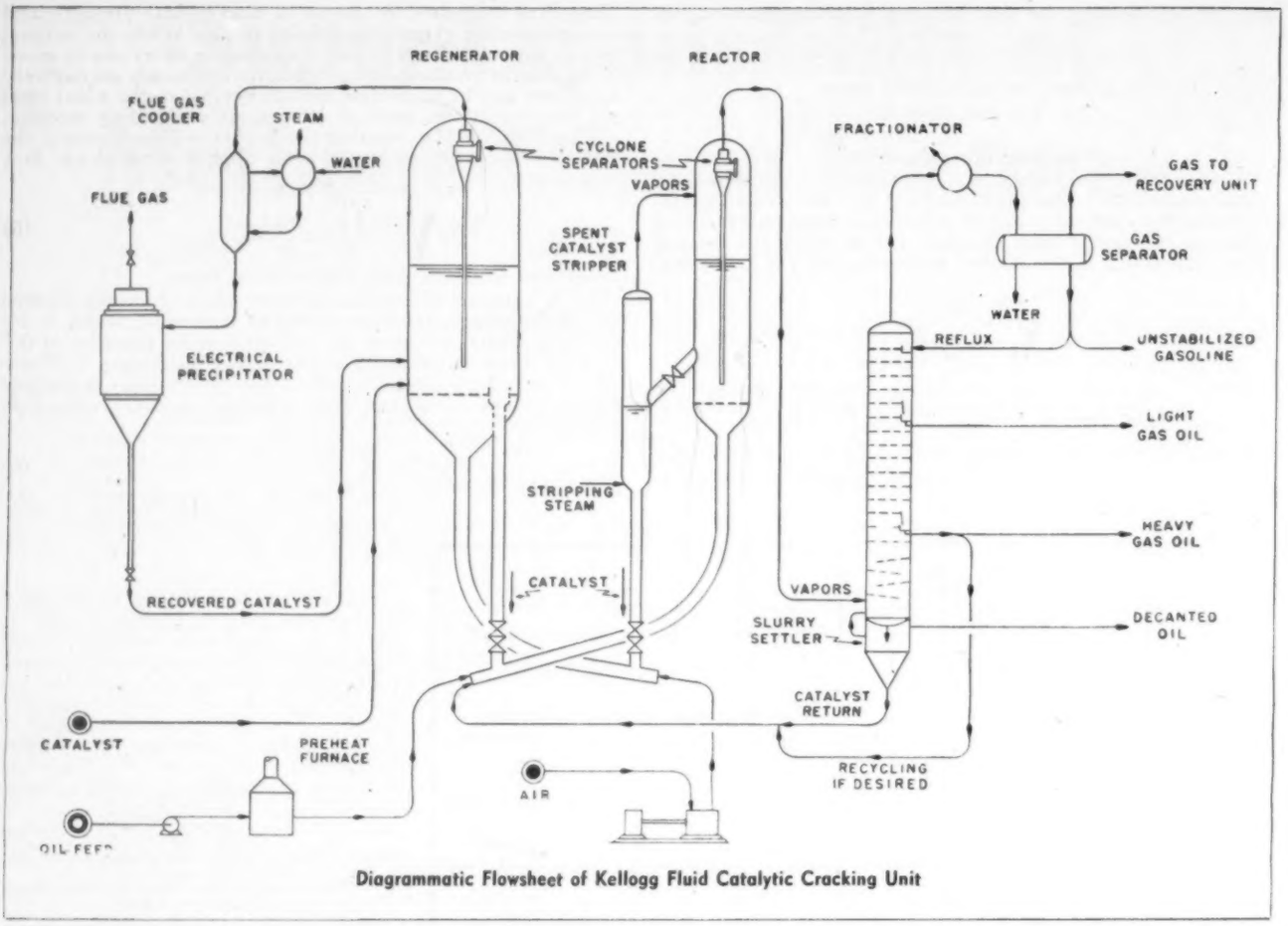


Diagrammatic Flowsheet of Kellogg Fluid Catalytic Cracking Unit

Small Fluid Catalytic Cracking Unit

THE M. W. Kellogg Company has announced, through its publication, "The Kelloggram," a new design for small-capacity catalytic cracking units intended to meet the needs of refineries with throughputs of 10,000 barrels of crude per day and less.

Catalytic cracking units of 4000 and 5000 barrels per day cracking capacity are now being constructed, and design work has been completed for 1700 and 2250 barrel units.

The Flowsheet of a typical 4000-barrel Fluid catalytic cracker is shown. Of interest is that the main structure of this unit requires an area of only 1650 square feet and that the reactor, regenerator, and precipitator are all supported at the same elevation, 69 feet above grade level. The compact layout and lower elevations represent a saving in structure requirements, and other savings over wartime designs of large units, since they allow elimination of elevators and special expansion and rotation joints in catalyst piping, and all vessels except the regenerator can be shop fabricated.

The latest designs provide improved stripping with less catalyst deactivation, by withdrawing spent catalyst to an outside stripper where it is brought into countercurrent contact wtih the stripping medium. A slurry settler is incorporated in the unit to allow withdrawal of the bulk of the heavy oil from the system and return the catalyst fines to the reactor. This settler is located in the base of the fractionator where it requires no separate equipment and has the additional advantage of increasing the catalyst settling rate by employing the full tower temperature to reduce oil viscosity. Also included in the design is a feed-preheat furnace which increases operating flexibility of the unit, and an electrical precipitator which allows the use of any and all tested types of fluid catalyst, natural and synthetic, while avoiding unnecessary loss of catalyst in flue gases.

OPERATION HOW TO DO IT MAINTENANCE

1. High-Pressure-Steam Valve Gasket Leak Repaired in Service

WHEN a flanged-bonnet forged-steel gate valve developed a gasket leak which daily increased the volume of wasted steam, the first thing suggested was "shut the refinery down." This would be expensive and consequently the last resort. To meet the emergency, a plant welder volunteered to make the repair while the valve was in service.

First he welded a high-pressure half-inch gate valve to the bonnet flanges of the leaking main-line gate valve. Welded to both flanges, the opening to the small valve bridged the gasket space and provided an escape for the steam during the following welding operation.

Starting at one side of the escape port, beads were run to join the flanges of the large valve. When the circumference of the bonnet had thus been welded, the smaller valve was closed. This normally should have confined the leak, but steam began escaping between the nuts and the bonnet of the valve. This presented another problem.

Cap or "acorn" nuts were obtained for all the bonnet bolts, to be used to prevent leaks between the nuts and bolts at the threads. The escape-port valve was opened again to release pressure of the escaping steam at the bolts, and one at a time the bolts were removed. Copper gaskets, similar to spark-plug gaskets, were placed on each bolt, under the heads and also under the cap nuts. When this operation was completed the small valve was closed, no steam escaped and the job was done.

The small valve welded to the flange served as escape port for the steam while the flanges were being welded while the steam valve was in service. Closing the small valve was the final step in stopping the leak.

Win a Bond

EACH month the operating personnel in the refining, cycling and natural-gasoline plants determine the winner of a War Bond, maturity value $25.00.

Superintendents, assistant superintendents and foremen (subscribers as well as non-subscribers) become a jury to select the most practical contribution to this department on maintenance and operation. The editors rotate voting among men qualified to determine the rating.

This award is in addition to payment for the article. The methods of solving plant operation and maintenance problems come from the personnel of the industry. Items provided by Petroleum Refiner staff members will not be eligible.

Send contributions to Petroleum Refiner, P. O. Box 2608, Houston 1, Texas.

2. Backwashing Shell-Tube Condensers Increase Cooling Efficiency

OBSERVING gradual increase in temperatures downstream from certain shell-and-tube condensers, a maintenance foreman reasoned a method might be found for cleaning the condensers without shutting down the plant for an overhaul.

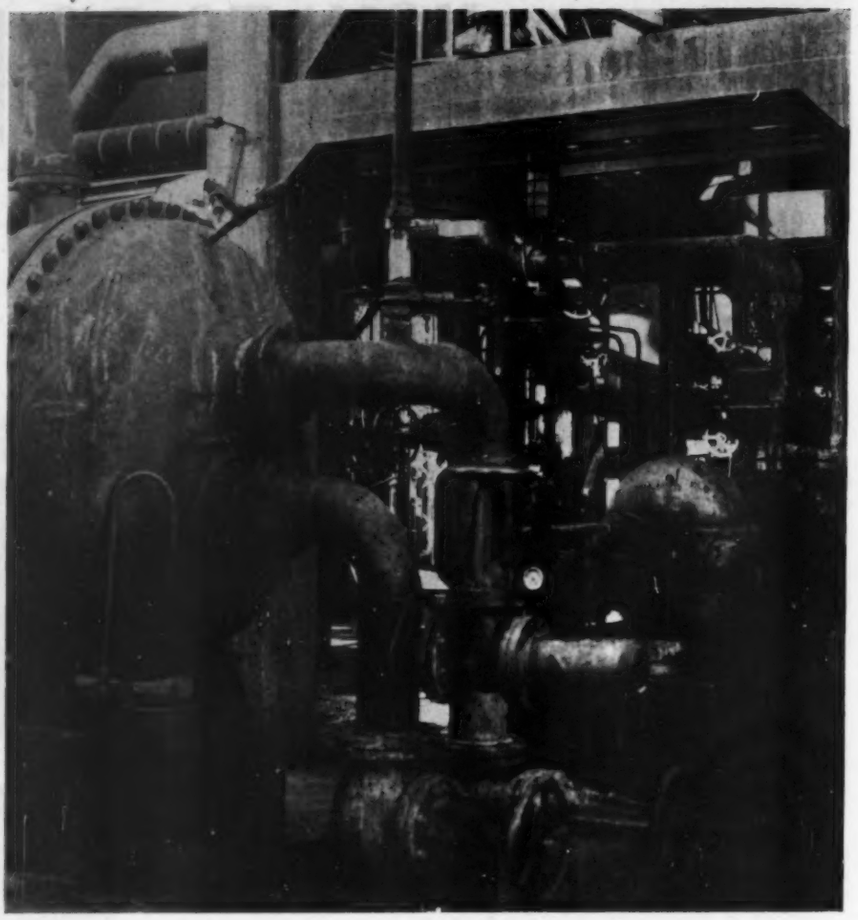
Cooling water is pumped through the coolers and condensers from an unusually large cooling-tower basin by a number of pumps. Discharge from the cooling units has a head equal to the height of the distributor piping reaching to the top of the cooling tower plus line friction added to the volume of water flowing from the coolers. If flow of water to an individual condenser is cut off by closing a control valve considerable pressure remains within the shell of the unit because of the back-pressure head in the distribution lines to the tower. Observing that a large quantity of water would flow backward through the cooler when the inlet line was disconnected between the control valve and the shell caused the foreman to reason that a sudden reversal of water travel would break down some of the sludge and soft scale. As an experiment, one unit was fitted with backwash connections by attaching a waste line between the shell and the valve in the pipe leading from the pumps. The tubes were not cleaned at the time of installing these fittings, and the unit was put back in operation without any change in adjustment of water flow or in volume of fluid passing through the shell.

Particular attention was given to the temperature of the fluid leaving the unit, and when a decided rise in operating temperature was observed the backwash method was given a tryout.

The gate valve in the line from the pumps to the cooler was closed and the waste valve opened, so that the full head of the discharge water in the system might flow backward through the tubes. The immediate visual result was a large volume of discolored water carrying quantities of sludge and scale which flowed out. Operating result was that temperature of the cooled liquid was lowered almost to the point of the efficiency of the cooler when newly overhauled by having the tubes cleaned in the conventional manner.

More of the condensers were fitted with backwash connections and results have been highly satisfactory. To increase turbulence in the backwashed water, an additional innovation was tried. An air line was attached to the outlet pipe on the condenser so that air under high pressure was admitted along with the reversed flow of water. This resulted in greater quantities of the scale and sludge being dislodged, with accompanying increase in transfer efficiency.

After the first unit was tried out and the result found to be worth the expense of making the connections, all new units in this plant are fitted with such backwash connections, and an additional waste line added. This other waste connection is attached to the outlet line so that when water flow is returned to normal direction after backwashing, sludge dislodged by the again reversed flow is discharged into the drain instead of being allowed to flow to the tower.



Connection on water line to dispose of water when backwashing the condenser. The connection in upper line is for compressed air to accelerate flow of water.

3. "Stinger" Attachment on Winch Truck Widens Material Handling Efficiency

OFTEN it is necessary for a small piece of equipment to be "spotted" at some point that is not attainable by the ordinary means of just backing the "winch truck" up to the "spot" because of interferring equipment, lines, buildings, etc.

When this particular situation confronted one truck driver, he obtained a length of 4-inch drill stem and made what he called a "stinger." This stinger had to have a collar on the base end so that his tiedown chains would not slip off, and it had to have a slot cut in the "stinger" end so a chain could be definitely anchored there and would not slip down the pole. The winch line was attached to the "stinger" at about the middle of the section.

Winch truck equipped with "Stinger"

As can be seen in the picture, the base of the pole was tied down near the cab and centered over the truck bed. The winch line by being attached to or near the center of the pole permitted the raising and lowering of the pole. The chain shown hanging down at the "stinger" end of the pole was used to attach the materials for which movement and placement were required. By having this "stinger" attachment it was quite possible to raise small equipment up and over low obstructions and "spot" it safely at any distance up to 12 feet from the closest point to which the truck could be moved.

Another method of use for the "stinger" is for the raising of materials to a higher elevation than is ordinarily obtained by the use of the normal "gin" poles. The method of attachment of the "stinger" in this case is somewhat different. The base of the pole is bumped down and tied or chained down in that position so that it can roll on its base as it is raised and lowered. The base is brought to rest on the framework of the truck just under the bed and at the point at which the trailer hitch is attached. If the truck is not already provided with sufficient and properly positioned "framework" in the nature of either truck chassis or trailer-hitch attachments, it takes but little time to weld a "socket" into the truck frame just above the

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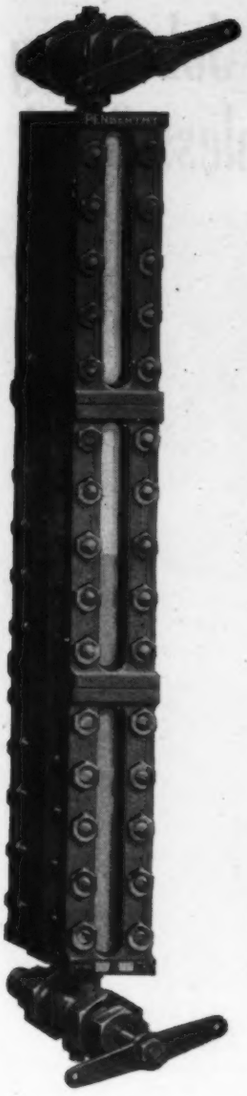

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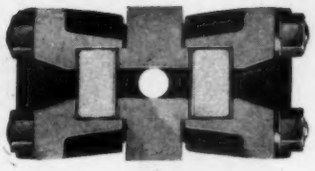

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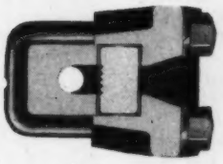

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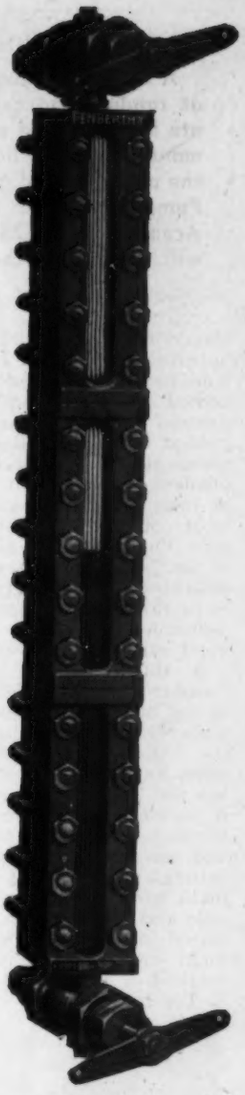

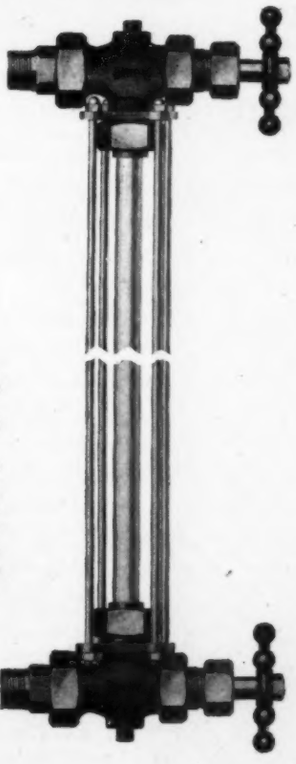

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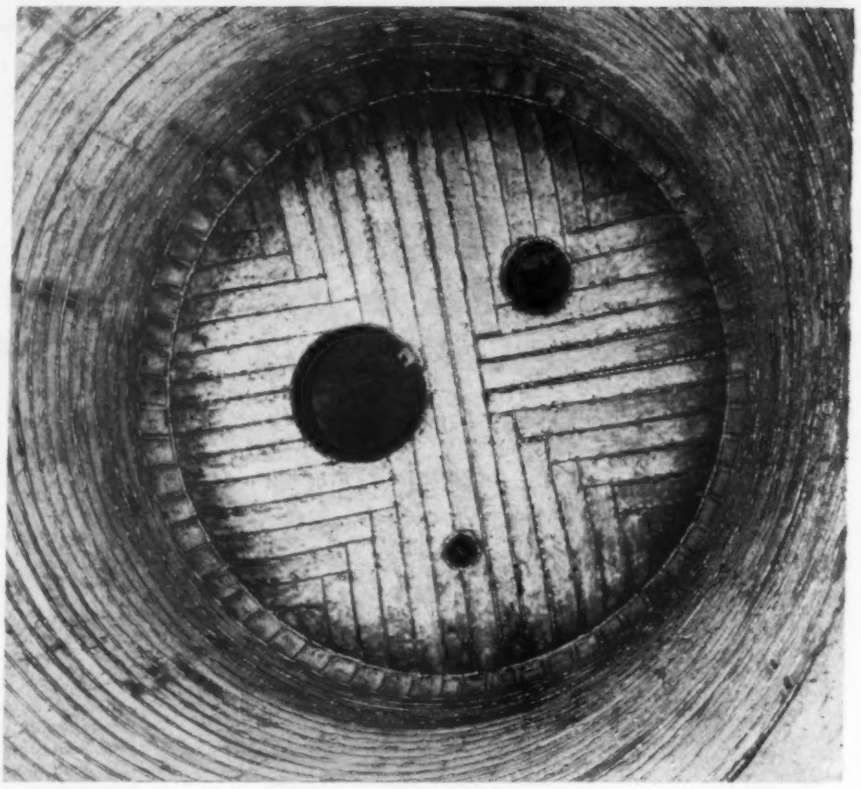
THE WINNER

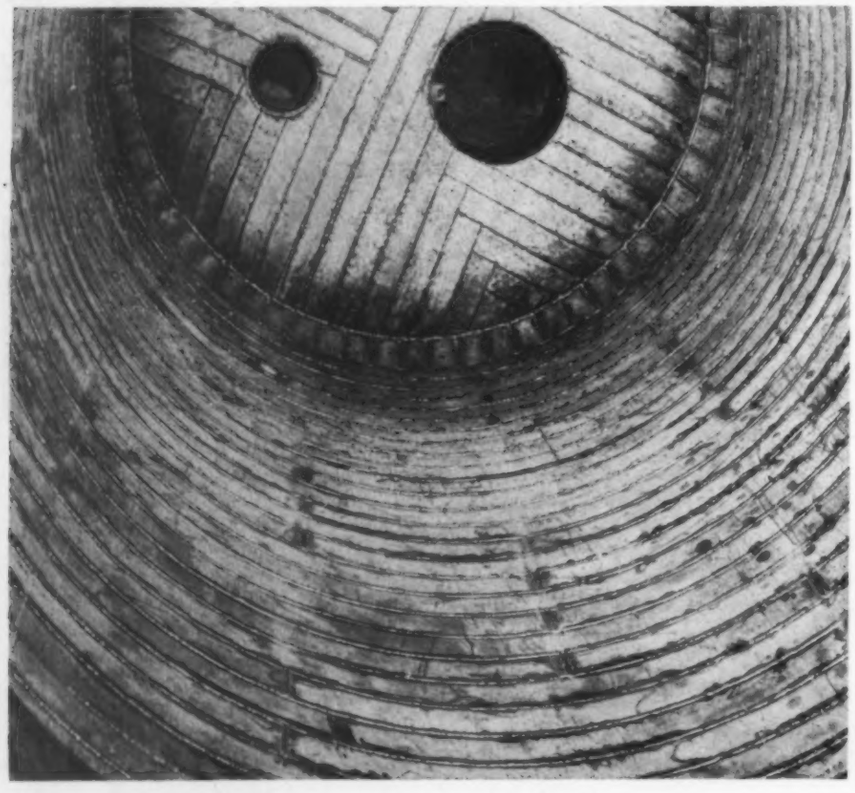
A number of readers selected at random and asked to evaluate items printed in this department in April have indicated the award should go to Item 5—Pump Discharge Line Support. Accordingly, a $25 Victory Bond will be sent to the contributor.

trailer hitch. This socket by providing a positive rotating base for the foot of the pole permits the winch line to be attached as in the previously described method of connection to the "stinger" pole at or near the middle. The spot to which the winch line is attached is dependent on the weight of the material to be raised, and the angle of the "stinger" is of course dependent on that variable also. The chain then provided at the end of the "stinger" is used as before as the attaching medium between the material to be raised and the pole. The pole is of course when using this method of attachment raised and lowered with the load.

A third method of attaching the "stinger" is to set the base of the pole in the "socket" provided just above the trailer hitch, raise the pole up against the "A" frame or normal winch truck poles and while the winch line is holding the "stinger" up in this position tie it securely into place with chains and boomers. The winch line is then cast off and run up the "stinger" thence down through a block. This method of attachment provides a lengthened stationary pole and the load can be picked up and raised into position without any movement of the pole whatsoever. This method of attachment is to be preferred in the movement of near capacity load.

4. Plant Welder Does Good Job Lining Flash Chamber With Stainless Steel





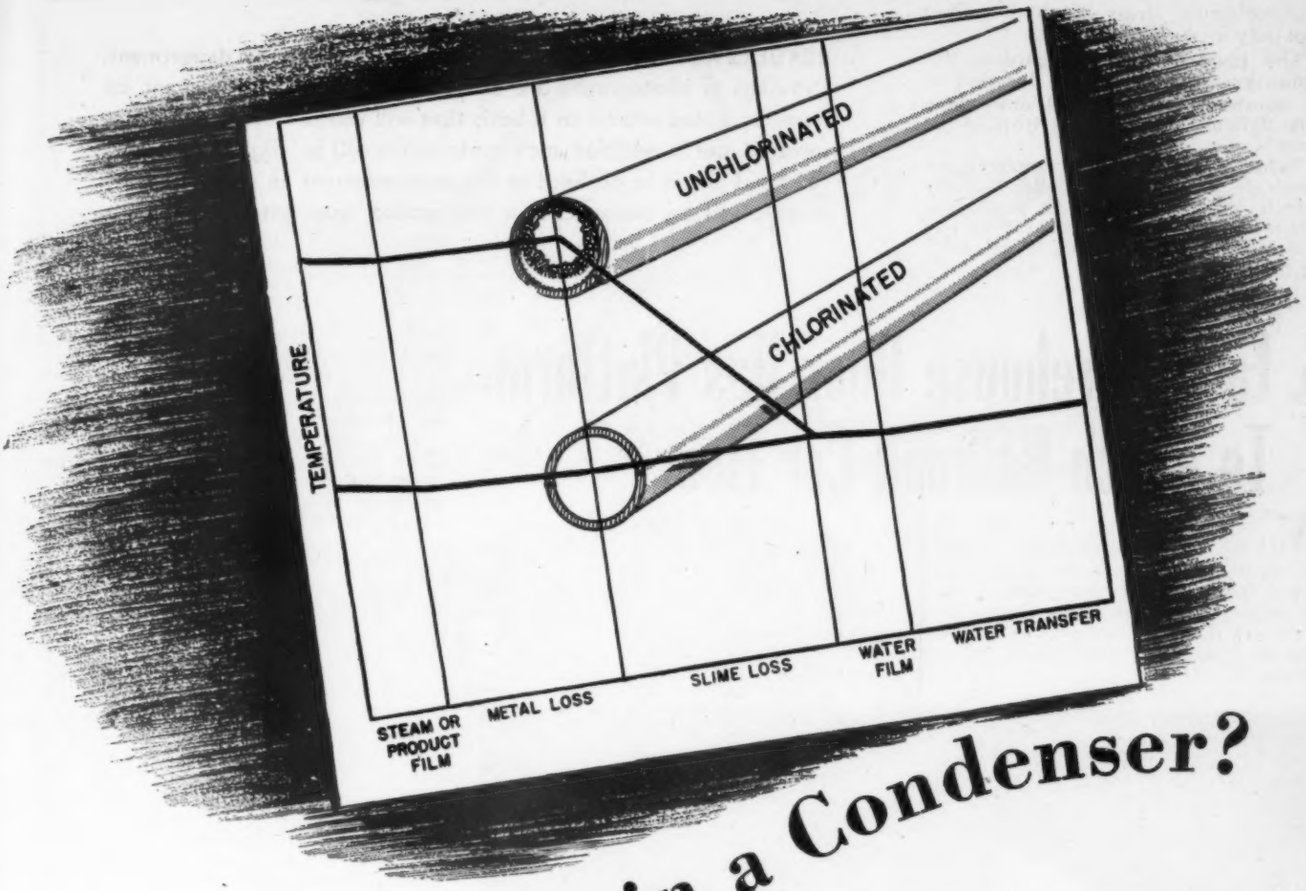
Two views of stainless strip lined vessel

ABOUT a year ago, relates I. T. Thornson, plant engineer for Naph-Sol Refining Company, Muskegon, Michigan, the ganister lining in the plant's 7x33-foot flash chamber was in such bad condition that it had to be removed. The tower was relined with ganister gunited into expanded steel grating, with the exception of the upper 10 feet and dome which was left to be lined with a stainless-steel strip liner at a convenient time in the not too distant future.

"Early this spring," Thornson continued, "we found that we had the time on hand to go ahead with the stainless-steel liner, and as the photographs indicate, a very satisfactory job resulted.

"In operation, temperature in the tower ranges from approximately 850° F. inlet to approximately 780° F. outlet, which allowed us to apply a 4-inch-width strip. We used Type 405 11½-13 percent chrome, 14-gauge, strips; welding rod Type 310 25-20 nickel, 3/32 and ⅛-inch diameter.

"Our welder, William Wright, could be depended upon to make a first-class job, as he has had a world of experience in all methods of welding, and much of this experience on stainless-steel applications. Therefore, we decided that on applying the horizontal strips to butt adjacent strips against the weld beads of previously applied strips, which resulted in a saving of one third on the horizontal welding. The knuckle and dome strips were welded along edges, and the final filler bead then applied to cover the bare tower wall exposed between these strips.



What Happens in a Condenser?

With cooling water chlorination there's just one answer — heat transfer. Without chlorination, however, there are two. First, of course — though less efficient — there's heat transfer but second, there's rapid development of slime. Warm, water side surfaces make ideal living quarters for slime-forming micro-organisms and as they grow condenser efficiency drops. Slime coatings so thin as to be almost invisible can result in loss of vacuum that sends cooling costs sky-high.

Continued operation of slime fouled condensers means higher fuel costs, increased cooling water requirements and reduced capacity. While plug cleaning means extra labor costs and costly equipment outage.

On the other hand, W & T De-Sliming Processes keep constant watch over cooling water systems — remove existing fouling and prevent the formation of bacterial slime by destroying the fouling organisms. Equipment stays in service — generally at better than guaranteed rating — and the resultant savings often pay for the chlorine control apparatus in less than a year.

Call the nearest W & T Representative today — he'll be glad to show you how W & T Chlorinators — engineered to your particular needs — can improve your condenser effectiveness.

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The horizontal strips required a filler bead only at the 4-inch joints.

"One point of interest regarding this application is the eccentric location of the manway, which caused more than usual difficulty in the layout work of the dome.

"When the work was completed we found we had used 160 pounds of the ⅛-inch weld rod and 125 pounds of 3/32-inch rod (less stubs). Lineal feet of welding totaled 2080 feet. Total welding time was 190 hours."

READERS ARE URGED TO CONTRIBUTE items to this department. Drawings or photographs are desired where practical. Payment for items accepted will be on a basis that will compensate for the time involved and in addition each contribution will be eligible to receive the bond award as outlined in the announcement on page 151. Jury awards will be announced in the second issue after publication.

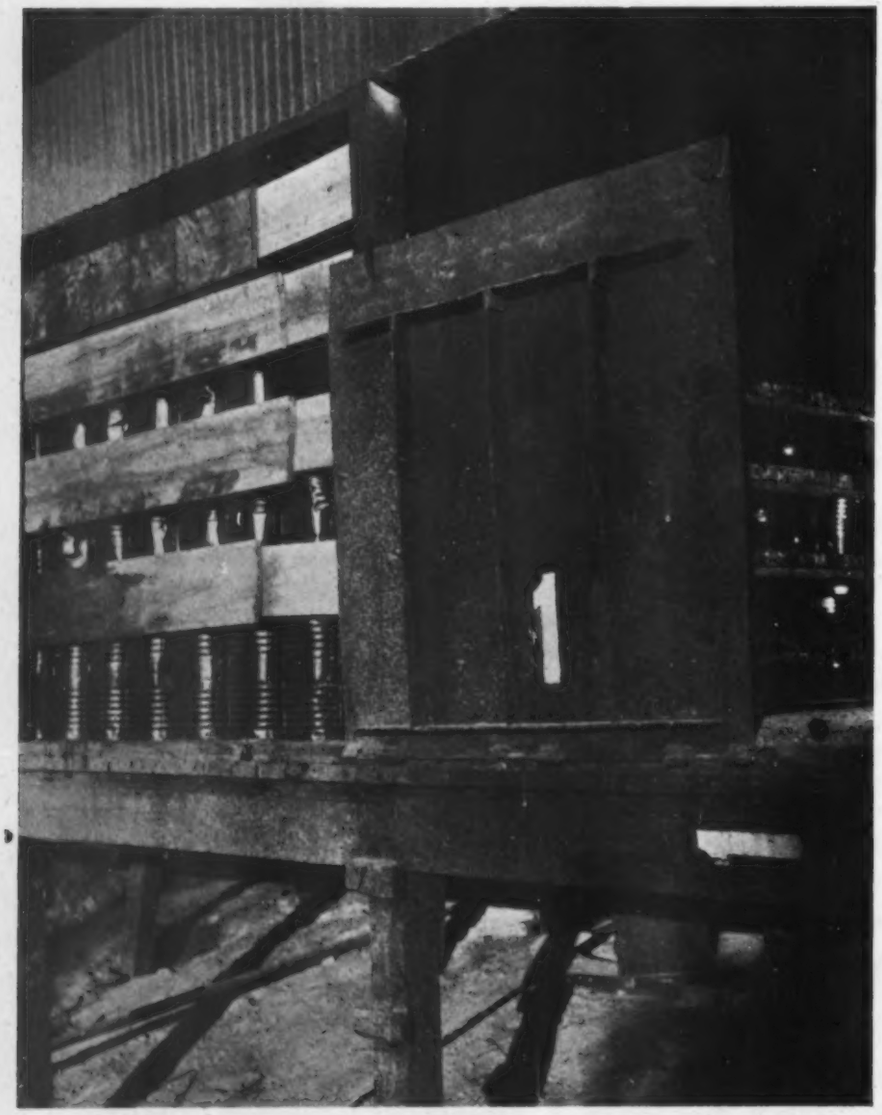
5. Each Warehouse Door Has Platform To Reach Railroad Car Floor

WHERE drummed products or those put up in bags or cans are to be transferred from the shipping room to waiting railroad cars, some type of bridge is necessary between warehouse and car floor to insure easy trucking of the materials.

One refinery provides a welded steel platform at each aisle, spacing these latter so that they come at intervals which match the door openings of coupled standard 50-foot freight cars. Where shorter cars are used, each must be spotted before a loading door. At the loading aisle three hinges are set on a steel plate extending well back across the timber floor. Each hinge consists of two bosses, carrying between them an 8-inch length of ¾-inch steel rod.

The steel platform likewise carries three bosses, so spaced as to come between the pairs on the floor plate. Holes in these bosses are drilled just large enough so that they will slide or turn readily on the ¾-inch rods.

When carried on these sliding supports, the platform may be moved sideways while in the up position enough to compensate for slight inaccuracies in spotting the car, and the platform then dropped to close the gap. Braces at right angles to each other, and so spaced as to clear the side of the car, afford the necessary stiffness to the platform without requiring excessive thickness of the steel plate with its consequent weight and bulk. The platform, when not in use, is held upright by a latch pivoted to the wall support of the warehouse, the latch engaging the upper edge wherever the sliding hinges may be placed on the rack below.



Reinforced steel platform for bridging gap for hand truck from warehouse to railroad car door

6. Guard Against Oil-Change Accident

CONTINUOUS reclaiming of the crankcase oil in large power units, such as compressor and generator-drive internal-combustion engines, provides a maximum of protection against fouling, overheating, or possible lubrication failure. Where this function is performed by a centrifuge or filter-press type of unit, to which is piped a portion of the crankcase oil for reclaiming while other oil is added, the human element must be considered, so as to protect against the possibility of the oil being drained from one crankcase and at the same time the supposed replacement oil is being added to another unit.

One superintendent protects against this hazard by installing pairs of valves in the oil piping so that when the suction line is connected to any certain crankcase the adjacent valve is opened on the oil-pressure line so that the oil from storage is fed in to replace that being drained out. As the valves are of the three-way type, it is impossible to open suction to more than one crankcase at a time, as the valve, when in the open position to the unit which it controls, also closes the line beyond that point. Thus, if the valves were accidentally aligned so as to take suction—and likewise to deliver replacement oil—to two or more units, the only oil actually being claimed would be drawn from the unit nearest the reclaimer or first tied in to the dual oil circulating pipe system.

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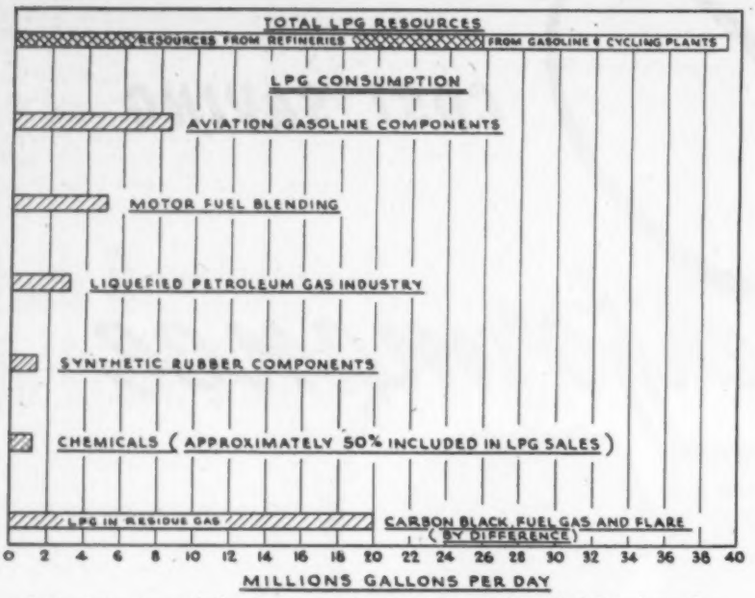
LIQUEFIED PETROLEUM GAS IN 1945


TOTAL LPG RESOURCES
RESOURCES FROM REFINERIES
FROM GASOLINE & CYCLING PLANTS
LPG CONSUMPTION
AVIATION GASOLINE COMPONENTS
MOTOR FUEL BLENDING
LIQUEFIED PETROLEUM GAS INDUSTRY
SYNTHETIC RUBBER COMPONENTS
CHEMICALS (APPROXIMATELY 50% INCLUDED IN LPG SALES)
LPG IN RESIDUE GAS
CARBON BLACK, FUEL GAS AND FLARE (BY DIFFERENCE)
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40
MILLIONS GALLONS PER DAY

Estimated average daily resources and consumption of Liquefied Petroleum Gas in first six months of 1945.

THE liquefied petroleum gas industry's initial rapid growth has been followed by a period, during war years, of very healthful consolidation.

Growth of the industry, particularly for domestic uses, in 1947 and 1948 should far exceed any previous two year period.

There is ample supply of butane and propane for the requirements of motor fuel, aviation gasoline, synthetic rubber, and chemical industries, over and above the requirements of the LPG industry. In fact, the potential supply far exceeds present demands of these industries.

Increased cost of production facilities and competition from other industries for the products will, over a period of time, probably increase the cost of propane and certainly increase the cost of butane to the LPG industry.

Leveling out the winter-summer ratio is the industry's best assurance of continued satisfactory supply and will serve to delay price increases brought on by competitive industries.

This paper was presented before the annual meeting of Liquefied Petroleum Gas Industry, Colorado Springs, May 27-29, 1946.

The authors, Mr. Oberfell is vice president in charge of research and development, and Mr. Thomas is manager of research, Phillips Petroleum Company, Bartlesville, Oklahoma.

The Lighter Hydrocarbons Have Taken On a Lot of Weight

G. G. OBERFELL and R. W. THOMAS
Phillips Petroleum Company

THE title which we have chosen, *"The Lighter Hydrocarbons Have Taken On a Lot of Weight,"* while somewhat facetious, is one whose inference is of vital importanceto every one who has an investment in, or is closely associated with, the liquefied petroleum gas industry. In this discussion frequent references will be made to the liquefied petroleum gas industry, and it may, therefore, be well to accurate define the term. For purposes of this discussion, the term "liquefied petroleum gas industry" is intended to include all phases of the production, transportation and distribution of propane, butane and various mixtures thereof for domestic, industrial and utility uses. Many remember the early days of the industry when the hard, energetic sales efforts of the industry for an entire year resulted in no more additional users of our products than many of your companies can now sell in a few weeks time. The contrast of "then" and "now" is indeed interesting. Twenty years ago the problem of the producers, who were interested in marketing liquefied petroleum gas, was primarily the development of a market for large quantities of propane and butane which were being wasted, or were going into extremely low priced fuel uses. Prior to this time natural gasoline was "weathered," allowing millions of gallons of propane and butane to escape into the atmosphere, and large flares for the purpose of disposing of excess propane and butane burned in gasoline plants and refineries. Before 1930, sale of a single car load of one of the products was considered as sufficient reason for sales managers to rejoice.

Sales promotion, advertising and technical and equipment advances by the entire industry during the 1930-40 period developed rapid public acceptance of the use of the products and sales showed a marked increase each year, even during the so-called depression years of this period.

By 1940 the industry had definitely reached the "grown-up" stage and the years of 1941 to 1945 inclusive can well be considered the years of consolidation. Prior to 1941 a very large percentage of distributors of LPG for domestic fuel uses had considered this type of use as a "means to an end" in securing profits from utilization equipment and appliance sales, without seriously considering the potential profit available through planned gas distribution service. During the war period many distributors, rather than depending upon appliance and equipment sales as their major source of profit, concentrated upon making the marketing of liquefied petroleum gas profitable; industries increased their use of the fuels for all types of industrial processes in the manufacture of war materials; and utilities expanded their use of liquefied petroleum gas to augment the capacities of their plants, overtaxed by wartime demands. Almost simultaneously with the consilodation of gas distribution, unprecedented acceptance of the industry by the public has placed the demand for liquefied petroleum gas service for modern, suburban and rural homes on an equal plane with the telephone, radio and automobile. Careful consideration of these facts certainly justifies the statement that *"The Lighter Hydrocarbons Have Taken On a Lot of Weight,"* and clearly indicates that the industry is at the threshold of its greatest period of expansion.

Sources of Supply of LPG

As you all know, liquefied petroleum gases come from three sources: natural-gasoline plants, cycling plants and refineries. To avoid troubles caused by the condensation of liquid hydrocarbons during the transmission of natural gas from the point of production to places where it is consumed, the heavier hydrocarbons are partially removed. Natural gasoline and liquefied petroleum gases are generally extracted in natural-gasoline plants near the gas source. It is customary to separate the extracted material into the desired grade of natural gasoline, and into butane, mixtures of butane and propane, and propane. The greater number of such cuts, the more fractionating equipment required.

A relatively recent source of LPG is from cycling plants, some of which utilize that physical phenomenon known as retrograde condensation. In certain underground reservoirs, many located on the Gulf Coast, high-pressure gas exists with little, if any, liquid in the formation. When the gas is brought to the surface and its pressure reduced, sizeable quanti-

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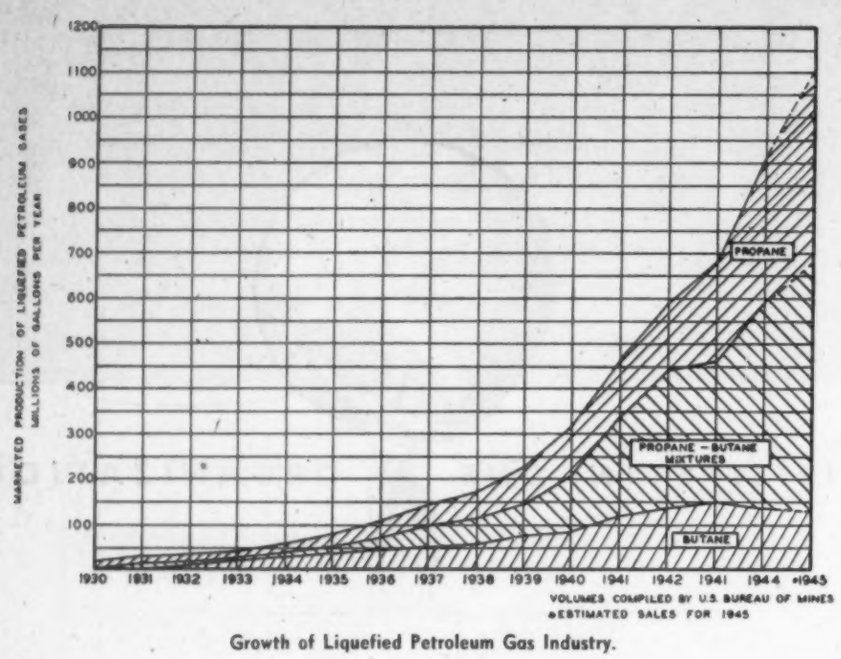

Growth of Liquefied Petroleum Gas Industry.

ties of liquid condense from the gas. The residual gas is then returned to the ground in order to maintain the reservoir pressure as nearly as possible at its original pressure, because reduction in pressure may cause liquid to condense in the formation. This operation of withdrawing gas from an underground reservoir and returning most of it to the formation has given rise to the term "cycling." The liquid material removed generally contains sizeable quantities of butanes and propane which are generally extracted and sold as LPG.

Another source of LPG is from the processing of crude oil in refineries. As a result of the various heating operations performed in refining crude oil sizeable quantities of light hydrocarbons are produced. From these light hydrocarbons liquefied petroleum gases can be separated.

Use of LPG During the War

Throughout this talk reference is made to the term liquified petroleum gas. Most of you think of this as butane and propane while actually a number of additional hydrocarbons may exist in the LPG. In the case of material secured from natural-gasoline and cycling plants only the paraffin or saturated series of hydrocarbons generally exists. In the paraffin series we have only one C_3, porpane, but two C_4's, butane and isobutane. In the case of refinery LPG, in addition to the hydrocarbons found in material obtained from natural gasoline and cycling plants, varying amounts of olefins (sometimes called unsaturates) occur. Of these the ones of interest are propylene and several butylenes. For simplicity, we use hereafter the terms butane and propane to refer to all the hydrocarbons in the C_3 and C_4 groups.

During the war large quantities of light hydrocarbons were used in the production of war materials. To fully appreciate the present supply-and-demand picture of LPG it is necessary to briefly consider the production and consumption of these products during this period. Large quantities of LPG were required in the manufacture of 100-octane aviation gasoline and synthetic-rubber components. The production of this aviation gasoline increased from a few thousand gallons per day before the war to over 20,000,000 gallons per day at the close of the war. Likewise the production of synthetic rubber which was only minor prior to the war reached approximately 800,000 long tons during 1945.

Since approximately a third of the aviation gasoline was produced from LPG, large quantities of these light-hydrocarbon gases were required for this purpose. The peak production of aviation gasoline consumed almost 9,000,000 gallons per day or about three times the average quantity of LPG used by our industry in 1945. A large amount of this LPG was obtained from thermal- and catalytic-cracking operations used in the refining of crude oil.

In the case of synthetic-rubber components approximately 50 percent were produced in 1945 from petroleum products. The two main components were butadiene and styrene, both of which are partially produced from LPG. It is estimated that during 1945, well over 1,000,000 gallons per day, a quantity of LPG equal to over a third of the average 1945 daily demand for all purposes of the LPG industry, was used in the production of synthetic rubber components. This demand for these light hydrocarbons has not decreased with the cessation of hostilities but rather has increased and it is expected that this demand will continue for several years to come.

It is evident that the war requirements for light hydrocarbons in the production of aviation gasoline and synthetic rubber increased from virtually nothing to between three and four times the quantity being used by the LPG industry. These hydrocarbons were obtained by increasing the quantity of crude oil being refined, through extensive use of the new and modified cracking facilities, installation of new natural-gasoline and cycling-plant facilities, and by installing new separation equipment for removing the light-hydrocarbon gases from gas streams which were heretofore sent to carbon-black plants, used in plant fuel-gas systems or in a few cases wasted. With the termination of hostilities the demand for light hydrocarbons in the production of aviation gasoline has greatly decreased. The requirement for the production of synthetic-rubber components, however, has increased because of the scarcity and high cost of ethyl alcohol, the principal alternate raw material. An interesting side light is that the quantity of crude oil being refined today is only slightly less than the quantity which was being refined during the war.

Present Demand for LPG

The sale of any material is with few exceptions to that market where it will command the greatest profit; LPG is no exception to this rule. When LPG was introduced in sizeable quantities it was more or less a secondary product, its production cost being its fuel value plus the cost of separating and purifying it. Today however, conditions have changed greatly. Instead of being used only for fuel purposes, LPG is being demanded in large quantities by several other markets which command prices higher than the LPG market.

Some of the most important markets in which LPG is used in large quantities are: motor gasoline blending, refining processes (polymerization, alkylation, etc.), synthetic rubber components, chemicals, carbon black, and plant fuel.

Most of you are aware of the fact that sizeable quantities of butane are blended in motor gasolines, the quantity depending to a great extent upon the season of the year, with greater quantities being so used during cold weather than during hot weather. Before the war a yearly average of 6 percent of the gasoline volume was butane. With the advent of increased cracking facilities the resulting gasoline generally has a higher vapor pressure than that produced before the war. This results in less butane being required in cracked motor gasoline. Gasoline produced by the operation of alkylation units will have, as a rule, a lower vapor pressure than that produced by cracking. This lower vapor pressure is increased by the addition of greater quantities of butane. While it is expected that some alkylation units will be operated for the production of motor gasoline it is rather difficult to estimate the future consumption as the process is rather expensive unless low-cost isobutane and butylenes are available. While it is expected that less butane will be required per gallon of gasoline sold than before the war, nevertheless approximately 1½ times the quantity of LPG used in 1945 by the LPG industry, still will be required in motor-fuel blending with the seasonal demand coinciding with the maximum LPG market demand. During the war sizeable quantities of propane were substituted for butane in the blending of motor gasoline. This substitution is not normally practiced except as an expedient. Therefore there is little commercial possibility of substituting another hydrocarbon for butane. When blended with motor gasoline, butane is worth slightly more than motor-fuel prices, which are considerably above current LPG prices.

Sizeable quantities of butane have been and will continue to be used for the synthesis of motor gasoline. If an octane-number race takes place in the marketing of motor gasoline, it is possible that a number of alkylation units will be operated in order to produce

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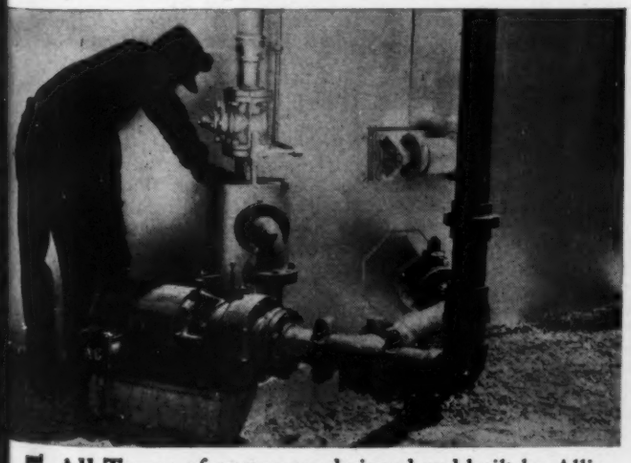

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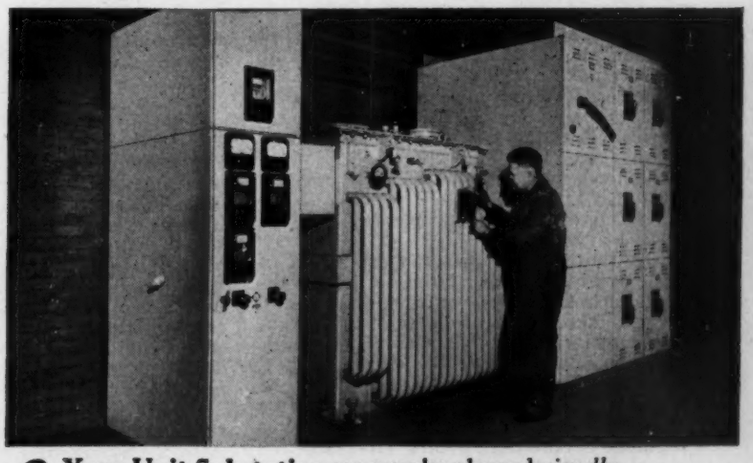

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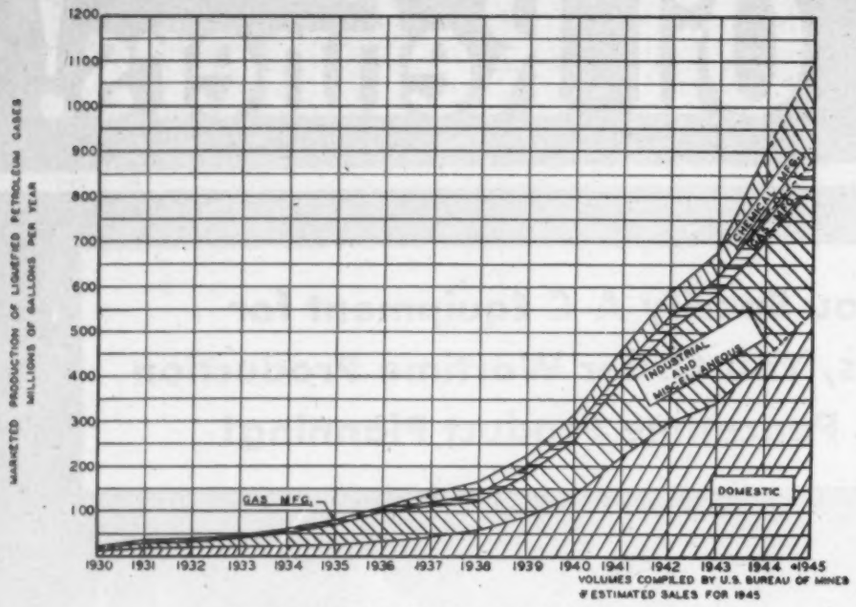

Growth of Liquefied Petroleum Gas Industry.

high-octane-number motor gasoline. The refinery alkylation unit is a means whereby isobutane and C_3, C_4 and/or C_5 olefins are converted chemically into a high-quality motor or aviation fuel ingredient. It is rather difficult to estimate what the demand for C_4 hydrocarbons would be for this purpose. It is possible that between 2,000,000 and 4,000,000 gallons per day of C_4's will be required for the postwar program of synthesizing motor fuel and aviation ingredients.

It is not expected that the C_4 demand in the production of synthetic-rubber components will cease for some time. It is estimated to be in the neighborhood of 700,000 gallons of C_4 hydrocarbons per day. Propane is used extensively as a starting product for the production of ethylene for synthesis of styrene and may continue at about the rate of 700,000 gallons per day.

Light hydrocarbons, especially propane, are used in the production of chemicals. The more desirable olefinic feed stock as a rule is obtained from refineries, resulting in many new chemical plants being located adjacent to refineries. The quantity of light hydrocarbons being used for the production of chemicals is increasing steadily but still represents only 20 to 50 percent of the light hydrocarbons consumed by the LPG industry.

With the large wartime expansion of the synthetic-rubber industry, new types of carbon blacks were required and great increase in production of conventional blacks, coupled with some modification of their properties was necessary. Carbon black is very essential to the manufacture of tires. The introduction of butane and propane in residue gas going to existing plants increased the carbon black production. Since many carbon-black natural-gas contracts require a minimum Btu or minimum carbon-black yield per cubic foot of residue gas burned, butane and propane cannot be extracted beyond a certain point.

Large quantities of heat are required around natural gasoline plants and refineries. It is the usual practice to pipe residue gas produced in these plants to points where it can be utilized to liberate the required heat. If butane and propane are removed from this residual gas the resultant supply may be insufficient to meet the heating requirements, in which case natural gas or oil must be substituted, giving the extracted LPG a value equivalent to the substituted natural gas or oil plus the additional processing costs necessary to secure a marketable LPG product.

Present Resources and Present Production of LPG

It was estimated that during the war the average annual resources of C_3 and C_4 hydrocarbons were more than ten times the total 1945 consumption of the LPG industry. When it is realized that the consumption of the LPG industry increased tenfold in the last ten years (1936—106,652,000 and 1945—1,100,000,000 gallons) it is readily apparent that the LPG industry will have to grow enormously before it makes noticeable inroads into the potential LPG reserves. In fact, it hasn't made a dent yet. It should be remembered that a large amount of the potential LPG will have to be separated from existing streams and treated in order to produce a product which will meet purchase specifications. This additional separation and treatment would increase the cost of this added volume to a point where it will not be possible to obtain it at the current LPG prices. This will have a tendency to cause a gradual increase in average cost of LPG. This increase is expected to continue until the price of motor fuel has been reached, particularly with respect to butane.

One of the sources of supply which is rapidly growing is from cycling plants. Also a number of new natural-gasoline plants are being erected. The main disadvantage with natural-gasoline plants is that frequently their LPG production is so small that it is difficult to justify the installation of the necessary separation equipment. In the case of cycling plants, however the volume is large enough that LPG manufacturing facilities can be justified. Because of the place advantage of LPG produced at the point of use, all needed refinery LPG is used to meet local demands of the refiner before securing shipments from natural-gasoline or cycling plants. Some refineries will have an excess over their own requirements and this material is potentially available to the LPG industry at a price.

Future Supply of LPG

As previously indicated, the supply of liquefied petroleum gas is derived from two distinct sources: that from cycling and natural-gasoline plants which is only partly related to crude-oil production, and that from refining of crude oil. It is not expected that the quantity of crude oil processed in the United States will decrease appreciably below its present level. Indications are for some increase in crude runs as the availability of new automobiles increases. In fact our national motor-gasoline demand for the first two months of this year is higher than for a similar period in 1941 and over 20 percent greater than the first two months of 1945. We have no reason to expect a diminishing supply of LPG from refineries. Likewise, with the increased demand for natural gas it is expected that greater quantities of LPG will be produced at cycling and natural-gasoline plants.

A recent development which enters the future LPG supply picture is the so-called Fischer-Tropsch process, or variations thereof, which use natural gas as raw material for the production of heavier hydrocarbons. The production of motor-gasoline and other petroleum products by this method may yield sizeable quantities of butane and propane. Therefore installations of this process for the production of petroleum products are not expected to diminish the overall supply of LPG.

The quantity of butane which will be available for use as such or in mixtures with propane by the LPG industry will be depenedent directly upon the price offered. Our industry is in competition with the butane requirements for the synthesis of aviation and motor-gasoline, production of synthetic-rubber components, blending of motor-gasoline, and chemical manufacture. These competitive uses can afford to pay more than current LPG prices for much of their requirements. Therefore the quantity available for use by the LPG industry will be the difference between the demands of the higher-price markets and the production. Until the LPG industry is willing to pay motor-fuel prices for its butane, the supply for LPG uses will be seasonal and limited. Far-sighted marketers will not depend on butane for their long-term future requirements unless they are convinced of the profitability of paying a premium over the propane market. Of course practically everyone is now purchasing transportation, storage and utilization equipment for propane because of this long-term trend.

Investment Considerations

The requirements of industries competing for propane and butane and the large volume sales of the liquefied petroleum gas industry itself have created problems of production, transportation and storage. The producer or producer-marketer and the distributor or direct user because of these mutual problems are more closely associated than ever before. Liquefied petroleum gas is now a co-product and not a by-product in most producing plants. Cost of butane and propane production has steadily increased. Since the production of LPG is

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a continuous operation, sale of liquefied petroleum gas must be made on a regular basis with almost constant daily shipments. Failure to move the products as they are produced can only result in increased cost. Meeting the industry's peak demands at present price levels is becoming increasingly more difficult for producers, transporters and marketers.

Transportation, that all important link between the producer and the distributor or user has become a very important factor in the industry. At the present time there are approximately $17,000,000 invested in the special tank cars required to transport butane and propane, exclusive of the pressure cars in butadiene and chemical services, and exclusive of the millions of dollars invested in LPG transport and tank trucks. Based on the present efficiency of movement of cars, an average investment of approximately $5,000 in tank cars is required to deliver one car per month to a distributor or user.

Seasonal Load Variations

Giving serious consideration to the major factors of production and transportation, it is clearly evident that if the liquefied petroleum gas industry is to maintain its present position economically, seasonal peaks in the deliveries of fuel must, to a great measure, be eliminated. A seasonal peak occurs during the winter months of November, December, January and February, caused in part by a high demand for winter space heating requirements in the South. The transportation problem which results is further exaggerated by a general slow-up in transportation in the North. Possibilities for improving the situation include:

1. Increased domestic consumer's storage, especially where consumer uses fuel for winter heating.
2. More LPG storage as distributor's bulk plant and at industrial and utility plants.
3. Active sales promotion of summer uses.

Ample fuel storage is the only assurance of an adequate LPG supply at all seasons of the year.

Active sales promotion of summertime uses of propane and butane offers opportunity for increased profits for the distributor. Summer loads are attractive for the reasons that transportation costs are lower during the summer months, working conditions and labor efficiency is greater at this time and, consequently, a greater margin of profit can be realized on fuel sales.

Possibilities for increasing summer activities include flame cultivation, weed burning, farm product dehydration and motor fuel use in farm tractors and irrigation power units. Flame cultivation of cotton, sugar cane and other row crops will consume large volumes of propane and butane during 1946 and this use will undoubtedly expand many times during 1947 and 1948. Considerable research and development work has already been carried out by the LPG industry with manufacturers of farm tractors and power units to provide prime movers factory equipped for efficient, economical use of butane and propane; 1947 should see several thousand factory equipped liquefied petroleum gas units in operation. Dehydration of alfalfa, sweet potatoes and other farm products will require large volumes of LPG in future years.

THE MONTH IN THE INDUSTRY

Wichita Section ACS Holds Annual Petroleum Meeting

Chemists, chemical engineers, and industrialists of the Middle West participated in the eleventh annual meeting of the Wichita Section of the American Chemical Society, at Wichita, Kansas, June 6 and 7.

The meeting was opened with an address by Dr. L. C. Kreider, of Bethel College, Newton, Kansas. Dr. W. B. Burnett, of the University of Wichita Foundation for Industrial Research, spoke on "Trends in Industrial Technology," and Davis Read, of Universal Oil Products Company, presented a paper, "Processes for Octane Improvement." Thursday afternoon, E. T. Scafe, Socony-Vacuum Oil Company, Paulsboro, New Jersey, spoke on "Sulfur in Light Petroleum Products," and W. R. Pierce, Phillips Petroleum Company, Bartlesville, discussed "Uses of Propane and Lighter Gases."

Friday's session opened with a paper "Resistance of Some Nickel-Containing Alloys to Some West Texas Crudes" which was read by H. L. Bedell, White Eagle Division, Socony-Vacuum Oil Company, Augusta, Kansas, who assumed this assignment on short notice when it was found that the author, B. B. Morton, of International Nickel Company, would be unable to attend as scheduled. "Economic Considerations of Refinery Corrosion Problems" was presented by Dr. F. A. Rohrman, Kansas State College, Manhattan, Kansas.

Friday afternoon, R. E. Bland and H. D. Noll, Houdry Process Corporation, presented "Economics of Small Scale TCC Units."

Harold Vogtborg, president of Mid-West Research Institute, Kansas City, delivered an address, "Research Potentials of Petroleum," at a dinner meeting Friday.

New officers for the Wichita Section of the American Chemical Society include H. L. Bedell, chairman, while Dr. Kreider, the past chairman, assumes the place of councilor, succeeding B. H. St. John. Eldon Means, Wichita, succeeds V. W. Hatchett as vice chairman, and B. F. Hartman, Augusta, Kansas, continues as Secretary-Treasurer.

Gunn Named Director API Division of Refining

William T. Gunn has been appointed director of the Division of Refining of the American Petroleum Institute, it was announced in New York by William R. Boyd, Jr., president of the institute. The appointment fills a post vacant since retirement of Dr. R. P. Anderson on December 31, 1944.

Gunn, a Texan, attended Texas A. & M. College and North Texas State Teachers College before his graduation from the University of Texas in 1926. After one year as a high school chemistry instructor at Austin, Texas, he was employed by The Texas Company at Port Arthur in 1928, and has remained with that company until accepting his present connection with API. His assignments have included chemist in the research laboratory at Port Arthur, chief chemist at both Houston and Casper

WILLIAM T. GUNN

Works, and since 1943 assistant to K. G. Mackenzie in New York, where his work consisted to a great extent of research development and plant operation. During the war period he participated in the work of the technical advisory committee of the Petroleum Industry War Council.

And Now Our Apologies

In a letter William F. Lowe, secretary of Natural Gasoline Association of America, recites some of the difficulties of getting proper credit to California Natural Gasoline Association, which holds an undivided half interest in "Physical Constants of Paraffin Hydrocarbons," as printed in the May, 1946, PETROLEUM REFINER, page 244.

Just as others had failed, PETROLEUM REFINER failed to mention that this also is a standard of the California Natural Gasoline Association. It happened once and Bill Lowe apologized to George Tyler, secretary of CGNA. Then it happened again and another apology was made, again Lowe to Tyler. Then there was an instance of large type and small type as between the two associations and again an apology was relayed Lowe to Tyler.

This time we are making the bow for Lowe, who doubtless is becoming discouraged.

For the record "Physical Constants of Paraffin Hydrocarbons" is a joint standard of the two associations.

E. O. Bennett Associated In New Consulting Firm

E. O. Bennett, James O. Lewis and David G. Hawthorn, have formed a partnership as consultants in petroleum and production engineering and geology. The firm name is Petroleum Consultants, with headquarters at Houston.

Conventions

June
24-29—American Society for Testing Materials, annual meeting; Buffalo.

August
25-28—American Institute of Chemical Engineers, Western Section, San Francisco.

September
16-20—National Instrumentation Conference and Exhibit, Wm. Penn Hotel, Pittsburgh.
18-20—National Petroleum Association, Hotel Traymore, Atlantic City.

October
7-12—American Gas Association, Atlantic City.

November
11-14—American Petroleum Institute, annual meeting, Stevens Hotel, Chicago.

Indiana Standard Groups Exchange Technical Data

Research personnel of Standard Oil Company (Indiana) and affiliated companies met at Edgewater Park, Mississippi, during the week of June 13 for an exchange of technical information. More than 80 scientists, engineers and technicians heard 70 papers on a variety of subjects.

Dr. D. P. Barnard, associate director of research, told the gathering that scientific controls in the manufacture of motor fuels is becoming increasingly important as more efficient engines require specialized fuels. He named improved manifolds which affect volatility requirements and automatic transmissions as particular automotive changes which necessitate fuel improvements. A desalting process using Fiberglas has been brought through the pilot-plant stage and is now ready for a full-scale tryout, it was reported by Dr. C. R. Harte of the Whiting research staff. A paper by W. T. Herget of Pan American Refining Corporation described an electrical desalting method, which brings the salt content down to less than a tenth of an ounce per barrel.

Sulphur removal was discussed in several papers. In recent research on new catalytic methods for removing the sulphur from crude oil liquid yields of 100 volume percent or even higher have been obtained, according to Dr. R. V. Shankland. A new sulphur-removing process which sweetens gasoline in one step was described by Dr. Nathan Fragen.

Catalytic cracking operations have progressed so rapidly that they are already using a better catalyst than was employed during the war for high-octane aviation fuels, A. C. Hershey, chief chemist at Wood River refinery, said. Using the new catalyst increased returns from the process at Wood River alone amount to almost $1000 a day.

Dr. T. H. Rogers, associate director of research, predicted that new synthetic lubricating oils for special uses will result from study of wartime lubricant developments. "While high price will keep most of the synthetic oils out of the large-volume fields served by petroleum oils," he said, "we shall find synthetics being used for numerous special purposes such as instrument oils, where the pour point must be extremely low and the viscosity index extremely high. They

Scovill Tube News

Vol. 4 SCOVILL MANUFACTURING COMPANY, Waterbury 91, Conn. No. 2

Resistance to Erosion-Corrosion

It is characteristic of condenser tube alloys to form protective films of corrosion products which greatly reduce further attack. Some alloys develop continuous, insoluble, adherent, non-porous, self-healing films that are more resistant to erosion than others. Such alloys are selected for operating conditions suspected of accentuating the causes of tube erosion-corrosion. Aluminum Brass and Cupro-Nickel tubes have been found to have very high resistance to this type of attack. In some instances, however, the conditions are inherently so severe, even after all known practical remedies have been applied, that tube life of the most resistant alloy is short because of rapid and repeated destruction of protective surface films.

Mechanism of Erosion-Corrosion

The term Erosion-Corrosion has been selected to describe the type of attack generally discussed under the names of impingement attack, inlet-end corrosion, and air attack. Any continual abrasion of the tube surfaces by water containing entrained air or suspended solids, tends to break down, and prevent the formation of the protective film over the metal surfaces, thus exposing the clean metal to the progressive corrosive action of the circulating water. The attack is, therefore, combined erosion-corrosion — erosion removing the protective film, allowing subsequent corrosion of the clean metal surface. The seriousness of this action, which is a mechanical breakdown of the film, is dependent on the velocity of the water, the percent and size of entrained air bubbles, the presence of abrasive suspended solids and the composition of the tube alloy.

The attack may be localized at the inlet ends of the first pass (Fig. 1) or might extend over the whole length of the tube (Fig. 2) due to general erosion-corrosion of the metal.

The result of the action is a very irregular roughening and thinning of the tube wall.

In some cases the attack is concentrated in specific zones in the water box of a condenser, indicating that the causes are due to factors in the hydraulic cycle. Sometimes the occurrence of a rotating motion of the water in the inlet water box tends to form a low pressure area resulting in air bubbles of critical size collecting in the center of rotation. Attack is more severe on the tubes delivering this portion of the water. Other factors also result in localized tube failures; however, most failures of this type suggest a maintenance and routine inspection of the entire hydraulic system,

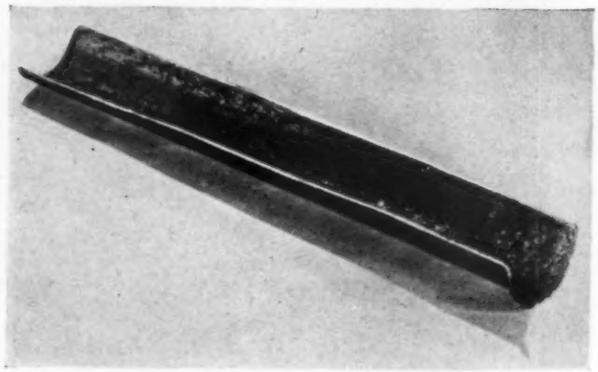

Fig. 1. Inlet End Erosion-Corrosion

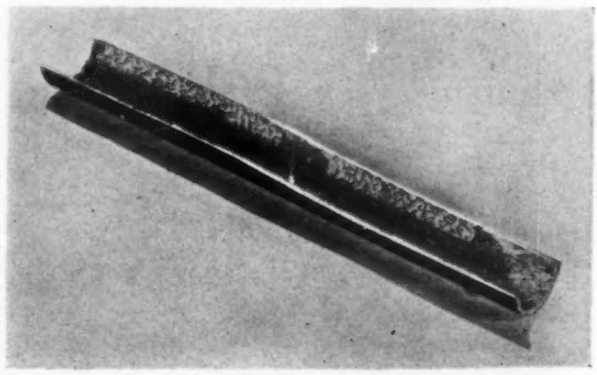

Fig. 2. General Erosion-Corrosion

starting at the intake water canal in order to determine the true cause of premature tube failure due to erosion-corrosion.

Mechanical Factors Contributing to Erosion-Corrosion

Air in the circulating water is in general the most direct cause of erosion-corrosion; however, any condition which creates air bubbles in water is a possible source of trouble. The source of bubbles may be from air entrained mechanically or from dissolved air released at low pressure areas or by turbulence. If adequate attention is given to the elimination of the source of released or entrained air, erosion-corrosion will be kept at a minimum. Some of the elements contributing to erosion-corrosion, that should be inspected for pressure differentials promoting the formation of pockets, turbulence and eddies, are included in the following list:

1. location of intake
2. pump suction bells
3. pump suction lift
4. non-vented air pockets
5. position of valve bonnets
6. pump thrust rings
7. pump gland seal
8. wear on pump blades
9. streamlining of reinforcing ribs, injection nozzle, inspection doors
10. venting of water boxes
11. projection of tube ferrules

Streamlining in the hydraulic system will minimize possible release of air. Belling of the tube ends to a proper hydraulic radius helps minimize localized turbulence (Fig. 3).

In general, erosion-corrosion depends on the presence of air or suspended abrasive solids in water

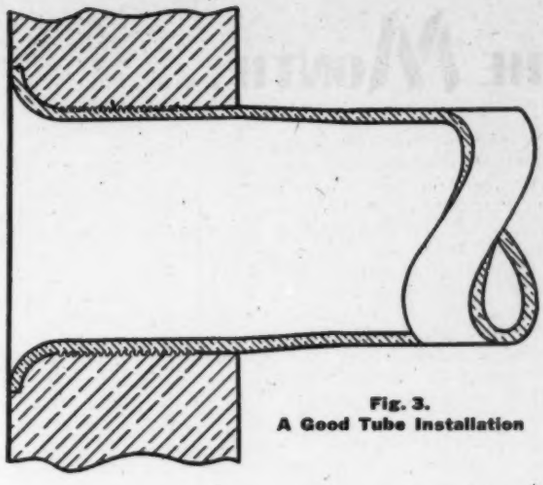

Fig. 3.
A Good Tube Installation

circulating at high velocities and is caused by conditions outlined above. For these conditions Cupro-Nickel or Aluminum Brass tubes normally would be considered most suitable.

Three Scovill Services

Service in Manuals, of which "Scovill Tube News" is a sample, consists of literature providing the latest, most authentic information* on condenser and heat exchanger tubes, which has its source in the broad experience of our engineers and the findings of our laboratories. *Service in Men* offers specialized consultation on individual tube application problems and suggestions regarding alloy selection and tube installation practice. *Service in Metals* includes the production of a broad range of tube alloys under laboratory control, which verifies that Scovill alloys selected conform to requirements of specifications.

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may also be used as the oil base for specialized greases."

Further progress in making gasoline from natural gas was reported by J. A. Phinney of Stanolind Oil & Gas Company and Dr. E. W. Thiele of Standard Oil Company (Indiana). "The process to be used will produce alcohols and other chemicals, as well as gasoline and lubricating oils, and is about ready for commercial development where special circumstances warrant it," it was said.

"The process is expected to supply all of the country's liquid fuel and oil needs when crude oil supplies are exhausted. It is of especial long-range interest because with some modifications it is also the most promising method for production of liquid fuels and lubricants from coal."

New chemicals will make it possible to plate metals two to eight times faster than before, it was reported by Dr. C. E. Adams of the Whiting refinery research staff. "These speeds have been made possible through the use of new sulfonic acids which give not only faster plating but also brighter finishes. The new acids have the additional advantage that they can be used over a wide range of operating conditions and are therefore more 'foolproof' than any previous electroplating bath."

Other possible uses for sulfonic acids include its use as a catalyst and where a strong acid is needed but where the oxidizing characteristics of sulfuric acid render it unsuitable.

The war plants used for making toluene are a tremendous source of new chemicals, Dr. R. J. Lee of the Pan American research laboratories reported. He stated that chemicals of many varied needs can be made by further reacting the products manufactured in peacetime operation of the toluene unit.

"The new materials are expected to find application as plasticizers and in electrical insulation, detergents, insecticides, fungicides, and organic chemicals manufacture," Dr. Lee said. "They can be used as partial or complete replacements for plasticizers which are twice as expensive, and they will, therefore, permit wider use of plastics for applications from which they would otherwise be barred by the high cost of the plasticizers which have hitherto been necessary."

Manufacture of high-quality varnishes from petroleum may be possible in the future, it was predicted by Drs. P. L. Brandt and L. M. Adams of Pan American, who reported experimental varnishes now made in part from petroleum have excellent water resistance. Similar petroleum products are also useful in paints and linoleum binders, and may also replace or supplement present agents protecting against marine borers, it was said.

Dr. B. H. Shoemaker declared that new ways of making alcohol from petroleum may reach the commercial stage soon by further perfecting processes partially developed by Germany during the war. The processes would be low cost and would make available higher alcohols which are not now commercially available.

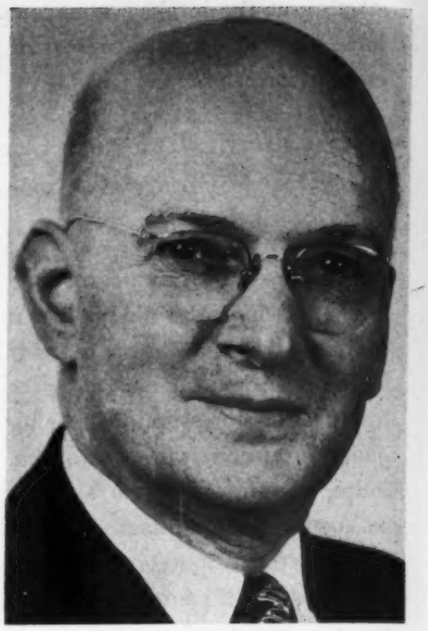
A new type of packing which may greatly reduce the height of towers in refineries and give better results was reported by William Kaplan of Pan American. "With this more efficient packing at lower cost," he said, "there will be considerable increase in the number of especially tailored products which can be made in existing equipment."

Other new developments reported include a new research tool for evaluating burning oils, new developments permitting better yields from oil wells, and new production methods arising from use of the electron microscope.

Shell Makes Calderwood Manufacturing Manager

A. H. Calderwood has been appointed manager of the manufacturing department of Shell Oil Company at San Francisco, where he replaces Dr. Monroe E. Spaght, whose appointment as vice president of Shell Development Company was announced recently. R. W. McOmie succeeds Calderwood as manager at Wilmington refinery, and L. R. Goldsmith takes McOmie's place as superintendent of that plant.

Calderwood joined the company in 1923 as engineering inspector for the purchasing department in Los Angeles. In 1932 he was appointed assistant manager of the refinery at Martinez where later he was manager from 1938 to 1942. The company's wartime expansion at Dominguez, including construction of the catalytic cracking plant and toluene plant, were carried out under Calderwood's management.



A. H. CALDERWOOD

Warren Corporation Buys Hanlon Group Properties

Through purchase of capital stock, Warren Petroleum Corporation has acquired Hanlon-Buchanan, Inc., and associated companies, for a consideration in the neighborhood of $12,000,000. The two organizations, headed by William K. Warren and E. I. Hanlon, respectively, both have headquarters at Tulsa. The six Hanlon companies involved are Hanlon-Buchanan, Inc., Henaghan & Hanlon, Inc., Hanlon Gasoline Company, Hanlon Gasoline Corporation of Texas, Hanlon Pipe Line Company, and Smith Brothers Refinery Company. These companies owned and operated natural-gasoline plants producing 75,000,000 gallons, and marketing facilities handling more than 250,000,000 gallons of natural gasoline annually; tidewater terminals with storage for tanker loading; 150 tank cars; oil properties in North Texas and Oklahoma producing over 3500 barrels daily, and large acreage of developed and undeveloped leases.

Prior to the purchase, Warren Petroleum Corporation and affiliates operated natural-gasoline plants with over 200,000,000 gallons daily capacity, and marketed more than 500,000,000 gallons annually, its tank fleet including 544 cars. Its tidewater terminals had storage for 34,000,000 gallons. The company owns substantial oil acreage and currently has about 600 barrels daily crude oil production.

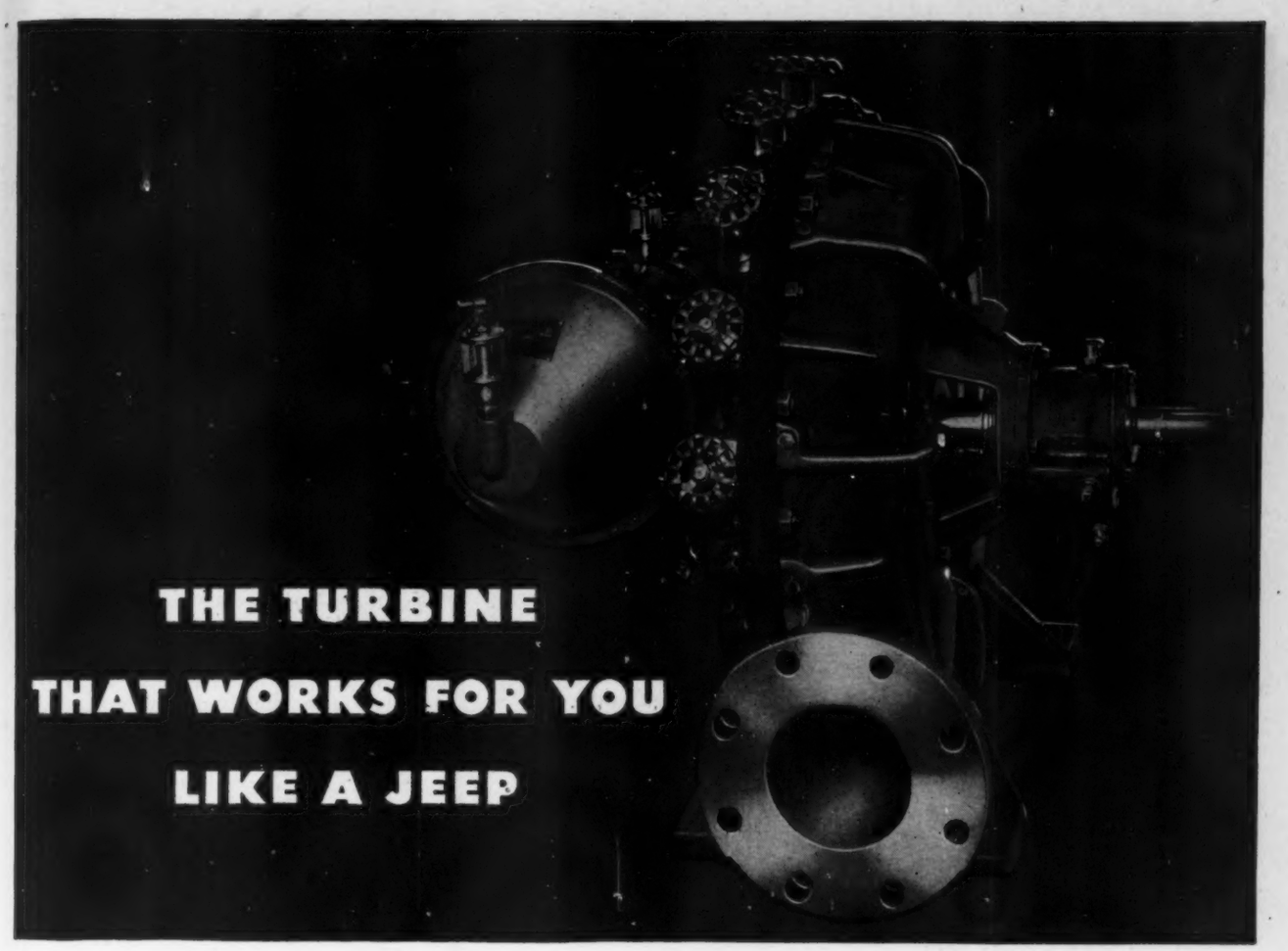
Warren Petroleum Corporation will retain the key personnel of the purchased companies. Ray E. Miller, vice president in charge of sales for Hanlon-Buchanan, will become a vice president of Warren Petroleum Corporation, of which J. A. LaFortune continues as executive vice president. J. H. Boyle, president of Hanlon Gasoline Company and of Hanlon Gasoline Corporation of Texas, will be vice president in charge of crude oil and

Trends of Operations and Changes in Stocks

Figures on crude stocks are from Bureau of Mines weekly reports; all others from American Petroleum Institute weekly reports, which are estimates on Bureau of Mines basis.

(All figures in thousands of barrels—add 000)

Trends in Week Ended:	Crude Oil			Gasoline		Gasoil and Distillate		Residual Fuel	
	Production Daily	Runs to Stills Daily	Stocks Week End	Production Weekly	Stocks Week End	Production Weekly	Stocks Week End	Production Weekly	Stocks Week End
1945:									
January 27	4,727	4,756	221,310	14,957	88,223	4,843	33,561	9,252	51,119
February 24	4,777	4,803	219,351	15,500	95,972	4,958	28,753	9,084	46,713
March 31	4,781	4,677	223,782	14,644	98,758	4,548	26,889	9,184	41,745
April 28	4,805	4,780	223,474	14,633	94,068	4,636	28,273	9,379	39,813
May 26	4,887	4,950	222,831	15,194	89,121	4,667	29,184	9,670	38,548
June 30	4,903	4,999	220,781	15,546	86,472	4,910	32,213	9,077	40,488
July 28	4,930	4,996	218,507	16,106	86,008	4,598	36,071	9,586	42,283
August 25	4,892	4,931	211,813	15,986	84,693	4,960	39,782	9,356	46,201
September 29	4,357	3,812	222,387	11,913	79,552	3,940	43,689	7,047	46,853
October 27	4,273	4,838	224,230	15,530	74,335	5,159	43,472	8,691	45,943
November 24	4,469	4,648	219,363	15,681	83,184	4,802	45,258	8,800	47,474
December 29	4,474	4,729	218,918	14,546	95,205	5,055	36,651	8,765	42,447
1946:									
January 26	4,626	4,553	220,544	13,622	107,737	5,720	29,498	8,411	39,722
March 2	4,726	4,779	229,430	13,871	104,462	5,888	25,148	8,634	38,441
March 30	4,425	4,684	221,214	13,896	104,715	5,357	28,240	8,738	37,746
April 27	4,672	4,685	221,689	14,228	99,631	5,568	30,466	9,204	39,404
May 25	4,759	4,857	222,214	14,322	95,769	5,463	32,973	8,908	43,368



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THE MONTH...

natural-gas operations. E. I. Hanlon and D. E. Buchanan, the latter president of Hanlon-Buchanan, Inc., have not announced their future plans.

Warren Petroleum Corporation was organized in Tulsa in 1922, and was a marketing company until 1935 when it acquired the gasoline department of Amerada Petroleum Corporation and added gasoline manufacturing to its operations.

The Hanlon companies started at Sistersville, West Virginia, in 1904, when E. I. Hanlon purchased the Daly interests in Henaghan & Daly, then changed to Henaghan & Hanlon. This company was the pioneer in manufacturing and marketing casing-head gasoline, and still operates eight natural gasoline plants in West Virginia. Moving to Tulsa in 1917, Hanlon joined Chestnut & Smith Corporation as vice president. Leaving that company in 1929, with Buchanan and Boyle he organized Hanlon-Buchanan, Inc., and other companies were added as operations were expanded. Among the subsidiaries, Smith Brothers Refinery Company operates two natural gasoline plants in Texas, rated at 55,000 gallons daily, and Hanlon Gasoline Corporation of Texas has plants at Gladewater and Breckenridge, Texas, with combined capacity of 140,000 gallons of natural-gasoline products daily.

Koontz Heads Mid-Continent Petroleum Corporation

Fred B. Koontz, who has been vice president of manufacturing and a director of Mid-Continent Petroleum Corporation, has been elected president of the company to succeed Jacob France who becomes chairman of the board of directors.

D. Glenn Martine, general superintendent of the company's West Tulsa refinery, has been named manager of manufacturing. G. E. Winn succeeds as general superintendent, and will have E. M. Downs and N. B. York as his assistants. Harry Morton has been appointed process superintendent.

Koontz has been with the company since 1917, starting as a refinery technician. He became refinery superintendent in 1922, and has been vice president since 1928.

Cities Service to Build Catalytic Unit at Chicago

Cities Service Oil Company will construct a Fluid-type catalytic cracking unit with auxiliary processes for its East Chicago plant. The new facilities will increase plant capacity to 35,000 barrels daily. Auxiliary units and additions will include a feed preparation unit, a polymerization unit, gas recovery unit, enlarged steam plant, more laboratory space and additional tankage.

Design and construction will be under the supervision of The M. W. Kellogg Company.

Government Sells Utah Refinery to War Operator

Sale of the 100-octane aviation gasoline plant at Salt Lake City, Utah, to its wartime operator, Utah Oil Refining Company, for $4,148,300, has been authorized by War Assets Administration.

WAA declared it has three more re-

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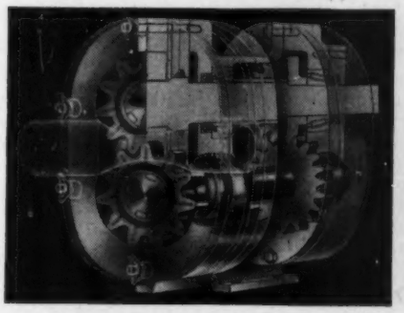

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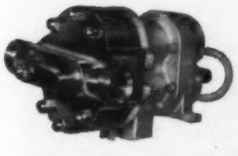

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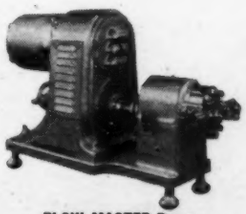

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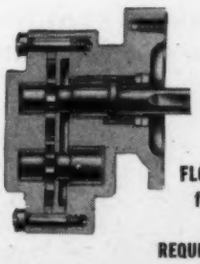

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THE MONTH...

fineries surplus and invited proposals for their sale or lease as follows:

Associated Refiners, Inc., plant at Duncan, Oklahoma, 5100 barrels 100-octane gasoline daily; Smith's Bluff, Texas, plant operated by The Pure Oil Company, rated daily capacity of 1200 barrels of aviation alkylate, and at Texas City, Texas, operated by Pan American Refining Corporation, rated capacity of 2540 barrels daily of isopentane.

Postponed API Directors Meeting Set for June 25

The deferred meeting of the board of directors of the American Petroleum Institute has been set by President William R. Boyd, Jr., for Dallas June 25-26.

Originally scheduled at Fort Worth May 28-29, the meeting was cancelled because of the railroad strike. When arrangements were made for a new date, it was found that hotel facilities would not be available in Fort Worth during June, but that the Adolphus Hotel in Dallas could take care of the meeting.

Boyd has advised the directors that "the board will continue in session until the docket is cleared."

Texas-Louisiana ACS Gulf Section Elects

V. A. Kalichevsky, consulting chemical engineer with Magnolia Petroleum Company, Beaumont, has been elected chairman of the Texas-Louisiana Gulf Section of the American Chemical Society. He succeeds W. W. Scheumann, Cities Service Oil Company, Lake Charles.

Vice chairmen are: A. R. Rescoria, chief chemist Cities Service Refining Corporation, Lake Charles; N. B. Haskell, director of fuels and fractionation, The Texas Company, Port Arthur; E. C. Daigle, chief chemist, Magnolia Petroleum Company, Beaumont.

Members at large were elected as follows: W. S. Miller, Mathieson Alkali Works, Lake Charles; T. B. Brantley, Gulf Refining Company, Port Arthur; H. N. Frost, The Pure Oil Company, Smith's Bluff; J. H. Stewart, Radiograph Laboratory, Beaumont.

Osborn Heads Continental Manufacturing Department

Harold G. Osborn has been elected vice president in charge of manufacturing of Continental Oil Company, to succeed Dr. Walter Miller, who retired March 1.

Osborn has been on the executive staff of the company's manufacturing department since November, 1921, when he was employed in the power division of the Ponca City refinery. The following year he was made office assistant to Dr. Miller, became assistant manager of the manufacturing department in 1927, and manager in 1935.

Osborn received his public school education in Kalamazoo, Michigan, and was attending Kalamazoo College when he left to join the Army Air Forces at the outbreak of World War I. He was

HAROLD G. OSBORN

commissioned in 1918 and served overseas. Following that duty he was a plantation manager in Louisiana until he joined Continental Oil Company.

Instrument Conference Plans Progressing

Over 1500 instrument men and engineers are expected to attend the first national instrument conference and exhibit of The Instrument Society of America, which will be held in the Wm. Penn Hotel, Pittsburgh, September 16-20.

Albert Sperry, president of the Society, in urging attendance at the "instrumentation for tomorrow" conference and exhibit, pointed out that now is the time to make plans for the long-awaited day when industry will aggressively resume production free of all restrictions.

The general chairman of the conference, R. J. S. Pigott, has arranged a very interesting program consisting of 15 sessions covering the following subjects: measurement and automatic control in industry, plant instrument department practices, inspection and gauging, scientific measurements, research in instrumentation, physical testing, etc.

Paul Exline, chairman of the exhibit committee, advised that up to May 1, 80 manufacturers had made reservations and advised that they plan to show many new and improved instruments and controls perfected during the war.

Chemical Exposition Dates Are Announced

The fourth National Chemical Exposition will be held in Chicago September 10 to 14, so as to take advantage of the semi-annual meeting of the American Chemical Society, September 9 to 13. The Chicago Section of the society will sponsor the exposition, which will be held in the Chicago coliseum.

Space already has been taken by 200 exhibitors, whose displays will cover the entire field of chemical products and chemical processes. The "chemical trail blazers" exhibit will be expanded for this show and the three dimensional method of presentation will be used in these displays.

Texas Pipe Line Plans Include Product Carriers

Both The Texas Company and Sinclair Refining Company are reported studying plans for pipe lines to carry gasoline inland from plants on the Texas Texas Gulf Coast. The Texas Company's line would be northward from Port Arthur, and Sinclair Refining Companys' line would be from Corpus Christi to Austin via San Antonio.

Humble Pipe Line Company is well along with construction of a products line from Baytown refinery to the Dallas-Fort Worth area.

Texas-New Mexico Pipe Line Company has initiated construction of a 16-inch crude-oil line to parallel its 12-inch line from Crane County in West Texas to Port Arthur via Houston. The new pipe will have rated capacity of 100,000 barrels daily, and with the existing 12-inch line will provide movement of 140,000 barrels daily of Permian Basin oil for account of the four companies—The Texas Company, Sinclair Prairie Oil Company, Cities Service Oil Company and Tide Water Associated Oil Company—which own Texas-New Mexico Pipe Line Company. Pipe for the line will not be available before late this year and completion is anticipated some time in 1947.

Calco Announces New Posts For Research Personnel

Calco Chemical Division, American Cyanamid Company, announces establishment of positions designed to give recognition to the professional accomplishments of its research personnel and to afford wide opportunity for their scientific services.

The first phase of the program was instituted in 1944 by establishment of the position of research associate to recognize high scientific attainments and wide experience in prosecution and direction of the research of the company. Research associates are relieved of the responsibilities for detailed administration of a regular unit of research in order to be available for important special assignments in the research department. They must have had not less than 20 years of professional experience since receiving the doctor of philosophy degree or its equivalent, and must have been in the employ of the company not less than 10 years, 5 of which were spent in directing or supervising the research work of others. The position is comparable with an executive position in research requiring similar experience and entailing equivalent responsibilities.

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When the vapor returns to the storage tanks, the membrane descends and air enters the space above it through the top vent.

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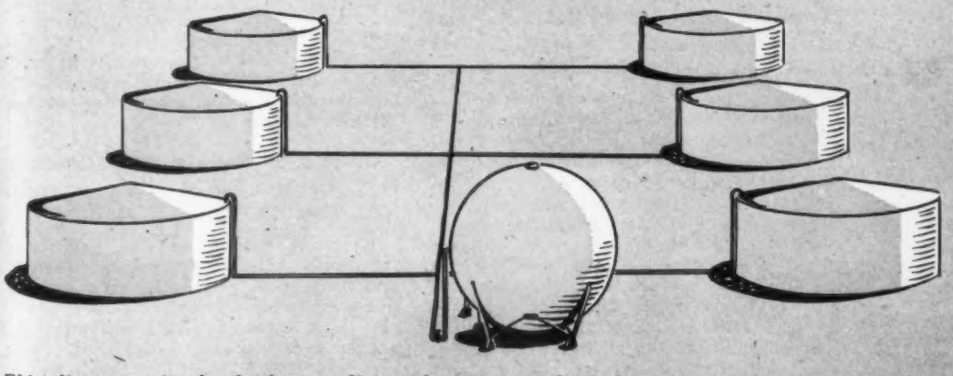

This diagrammatic sketch shows a Vaporsphere connected to the vapor spaces of six cone roof tanks. Vapor displaced from the tanks by daily breathing or by unbalanced filling and emptying flows through the lines into the Vaporsphere and later returns to the tanks . . . thus preventing evaporation losses.

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The abstracts here presented are selected from the current literature of science and technology to afford reference to fundamental information not easily available to all readers. Abstracts of articles appearing in readily obtainable trade journals are not included.

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Fundamental Physical and Chemical Data

Temperature-Density Relation for Gasoline-Range Hydrocarbons. J. GRISWOLD AND JU-NAM CHEW. *Ind. & Eng. Chem.* **38** (1946) pp. 364-67.

The temperature coefficient of density (a) in the equation, $d_4^t = d_4^{20} + a(t-20)$ for pure hydrocarbons from C_8 to C_{12} was correlated with hydrocarbon structure or type and molecular weight at temperatures near 20°C. by use of the formula, $-a = m(1/M - 0.002) + 6 \times 10^{-4}$, in which M is molecular weight and m is a constant depending only on structural type. This permits an exact conversion of d_4^{20} to API gravity whenever the type of compound is known. If the temperature range is wider, values of B in the equation, $d_4^t = d_4^{20} + a(t-20) + B(t-20)^2$, are calculated for the few compounds on which data of sufficient accuracy and range are available. The values of B also vary with structure but in an unknown manner. Charts are presented giving values of "a" for the normal paraffins, naphthenes, isoparaffins, olefins and aromatics, and values of B for the normal paraffins.

Extrapolation of the Experimental Critical Temperature of the Normal Paraffins. J. CORNER. *Trans. Faraday Soc.* **41** (1945) pp. 617-21.

The critical temperatures of the normal paraffins from propane to n-octane can be represented by four formulas, each with 3 arbitrary parameters, and with deviations of the order of 0.1°K. These formulas can be used to estimate critical temperatures of the higher paraffins with an uncertainty that is small at first but which increases to about 5 percent for $n\text{-}C_{25}H_{52}$.

Vapor-Liquid Equilibria in Three Hydrogen-Paraffin Systems. M. R. DEAN AND J. W. TOOKE. *Ind. & Eng. Chem.* **38** (1946) pp. 389-93.

The purpose of the work was to determine the solubility of hydrogen in a narrow-boiling mixture of isomeric dodecanes and in two relatively pure hydrocarbons—isobutane and 2,2,4-trimethylpentane—for over a range of temperature and pressure. Also the compositions of the equilibrium vapor phases were found, and a study made of the vaporization equilibrium constants of the components and the effect of temperature and pressure on these values. The solubilities of hydrogen in isobutane were determined for temperatures from 100° to 250°F. and pressures from 500 to 3000 psi. Solubilities in 2,2,4-trimethylpentane were found for temperatures from 100° to 302.5°F. and in a mixture of isomeric dodecanes for 200° and 300°F. with pressures ranging from 500 to 5000 psi. The compositions of the phases at equilibrium were determined. The solubility of hydrogen increases with temperature and pressure but decreases as the solvent molecular weight increase. The solubility of hydrogen follows Henry's law only in isobutane at 150°F. and lower. The hydrogen solubilities in the two heavier hydrocarbons increased more rapidly with pressure at low pressures than at high pressures. Correlation with data from the literature shows that hydrogen is more soluble in paraffins than in aromatics of similar molecular weight. Vaporization equilibrium constants were computed from the data for both solvent and solute. The constants vary widely with pressure and to a lesser extent with temperature. The constant for hydrogen increases with an increase in solvent molecular weight. The data are presented in considerable detail in three tables and eight figures.

Correlating Vapor Pressure and Latent Heat Data. L. SEGLIN. *Ind. & Eng. Chem.* **38** (1946) pp. 402-5.

A new method for calculating saturation temperatures, vapor pressures, and latent heats of vaporization is given, and is based on comparing these properties for any given material with the same properties of another material, the properties for which are known. The method permits the calculation of saturation temperatures within ± 0.5 percent, of vapor pressure within ± 4 percent, and of latent heats of vaporization to within ± 5 percent along the entire saturation line. The proposed method is a modification of the Gordon and Othmer methods, but is simpler to handle because it involves the use of simple arithmetic calculations only. A comparison of calculated properties with actual data is given for propane, methyl chloride, ammonia, n-pentane, isobutane, and carbon dioxide.

Correlating Equilibrium Constants. D. F. OTHMER AND A. H. LULEY. *Ind. & Eng. Chem.* **38** (1946) pp. 408-12.

Reaction-rate constants, equilibrium constants, solubility product constants, and ionization constants give straight-line plots on logarithmic paper against the vapor pressure of a reference substance at the same temperature, using the method of plotting developed for vapor pressures and several other physical properties of gases and liquids. This method can be conveniently used to correlate the limited number of experimental data available upon the change of the various types of equilibrium constants with temperature. A minimum of two experimental values is needed to fix the straight line over a wide temperature range. In addition the slope of the line can be used to obtain the heat of reaction at any temperature for any particular system. The heat evolved in the change of the polymeric structure of water, as indicated by the break in the ionization constant lines, is the same quantity of heat obtained for a similar break in the correlation for viscosity. The results of typical calculations are

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Dioleyl maleate
2- and 3-Ethyl thiophene
Δ^3-Hexenoic acid
Dioxirane
1,2- and 1,3-Dioxetene
s-Tetroxane
1,3,5,7-Tetroxocane
1,2,4,5,7,8-Hexoxonane
3-Indole-β-acrylic acid
2- or 4-Pyridone-3-sulfonic acid
Ethylene sulfide
4-Hydroxymercuri -2 -chlorophenol
4-Cyano-2-chlorophenol
2,5-Dichlorobenzoic acid
2,4-Toluene diisocyanate
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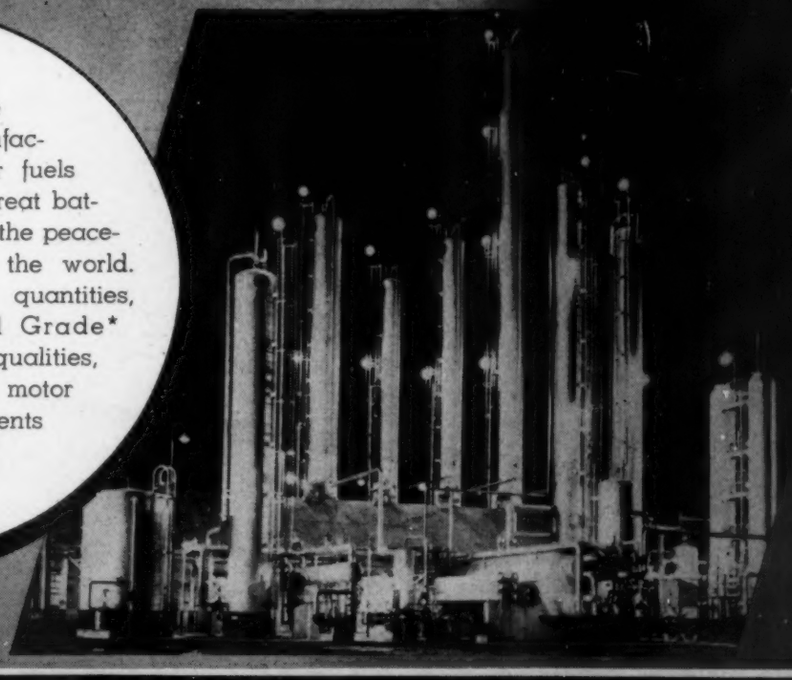

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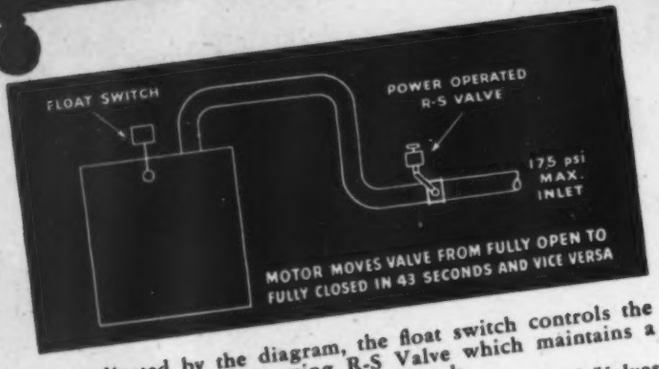
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presented in graphical form in eight figures. A bibliography of 16 references is included.

Molecular Weight-Physical Property Correlation for Petroleum Fractions. I. W. Mills, A. E. Hirschler and S. S. Kurtz, Jr. *Ind. & Eng. Chem.* **38** (1946) pp. 442-50.

The authors present several correlations of molecular weight with physical properties that cover the ordinary range of petroleum fractions. For fractions of 70-300 molecular weight, i.e. gasolines, kerosines, and light lubricating oils, boiling point and gravity are employed. The correlation gives good results for pure hydrocarbons of various types with an average deviation of 2.4 percent for 134 compounds studied. It also handles petroleum cuts satisfactorily. For lubricant fractions of 240-700 molecular weight the correlations are described for viscosity with gravity and for viscosity at 100° with viscosity at 210°F. The former are not, in general, applicable to pure hydrocarbons but give good results for most lubricant fractions, with the exception of Gulf Coast or California distillates above 350 molecular weight. With the use of a correction, the viscosity-gravity correlations give good results for these oils also. The correlation of viscosity at 100° with viscosity at 210° is in approximate agreement with the data for pure hydrocarbons of various types and gives good results for all types of petroleum fractions for which data are available. For petroleum waxes, melting point and refractive index at 80°C. are employed. The correlation is in good agreement with the data for the n-paraffins as well as for petroleum waxes of various types. The results of the study are presented in 15 tables and 9 figures, and a bibliography of 31 references is appended.

Isomerization Equilibria Among the n-Butenes. H. H. Voge and N. C. May. *Jour. Amer. Chem. Soc.* **68** (1946) pp. 550-53.

Isomerization equilibria among the three n-butenes were measured in the vapor phase at 200° to 630°C. Trans-2-Butene is the most stable isomer at the lower temperature, but 1-butene and cis-2-butene are nearly as stable at the higher temperature. The isomerizations were effected by flowing the n-butenes over granular catalysts in an electrically heated tube. Temperatures were held to within 3° of the desired value. Flow rates were chosen to produce essentially equilibrium conversion. Pressure used was atmospheric throughout. Equilibrium constants and free energy changes for the isomerization reactions are given. The results are compared with thermochemical measurements and with data derived from the third law of thermodynamics and spectroscopic observations. The side reactions observed were polymerization at the lower temperatures, cracking and isomerization to isobutene at the higher temperatures, and dehydrogenation at the highest temperature. The extent of the side reactions was below 20 percent, and often below 2 percent, except in the experiments at 630°C, when there was about 30 percent side reaction, chiefly dehydrogenation to butadiene. The author is of the opinion, however, that the equilibrium constants are not in error by more than

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10 percent. A bibliography of 12 references is included.

Molecular Weights of Viscous Hydrocarbon Oils: Correlation of Density with Viscosities. A. E. HIRSCHLER. *Jour. Inst. Petr.* **32** (1946) pp. 133-161.

The molecular weights of lubricating fractions were correlated with kinematic viscosities at 100° and 210°F., using a modified Keith and Roess chart, and with the density at 25°C. and viscosity at 210°F. By combining the two charts a correlation between the four physical constants was developed by means of which any two can be used to estimate values of the other two. Through the use of this chart, a simple equation was developed for calculating the molecular weight from viscosity data. The equation is applicable to oils with viscosity indices between −50 and +120. Published data on lubricant fractions were used, as well as on synthetic hydrocarbons in the lubricant range. The correlations were thus evaluated and compared with previously proposed correlations of molecular weights with viscosity data. The data on synthetic hydrocarbons indicate that the viscosity-density correlations are more sensitive to composition than the viscosity correlation. The viscosity correlation is therefore recommended when two viscosities are available. Consideration of many lubricant fractions indicates that the average composition is sufficiently uniform so that the viscosity-density correlations will give satisfactory results in most cases. Samples rich in naphthenes, however, should not be evaluated on the viscosity-density charts unless these charts are especially prepared for this type of oils. The results of the study are presented in 12 tables and 7 figures. A bibliography of 42 references is included.

Chemical Compositions and Reactions

Isomerization of Alkanes. I. Effect of Olefins upon the Isomerization of n-Butane in the Presence of Aluminum Halide-Hydrogen Halide Catalyst. H. PINES AND R. C. WACKHER. *Jour. Amer. Chem. Soc.* **68** (1946) pp. 595-99.

When pure n-butane was further purified by passing it over aluminum chloride granules and by redistillation, no isomerization of product occurred in the presence of aluminum bromide-hydrogen bromide catalyst, although this catalyst is effective in isomerizing commercial n-butane. It was found necessary to add various compounds that are ordinarily present in commercial butane as impurities in order to obtain effective isomerization. Olefins, air and water individually or collectively act as promoters for the isomerization of n-butane. These compounds may serve as a source of, or may cause the formation of, carbonium ions, which seem to be required to promote the isomerization of paraffins. The present paper is limited to a study of the effect of olefins upon the isomerization of n-paraffins. The addition of one part of olefin per ten thousand parts of n-butane is sufficient to promote isomerization. The effect of olefins, temperature, and concentration of hydrogen chloride upon the degree of isomerization is given.

Isomerization of Alkanes. II. Effect of Oxygen upon the Isomerization of n-Butane and n-Pentane in the Presence of Aluminum Bromide and Aluminum Chloride. H. PINES AND R. C. WACKHER. *Jour. Amer. Chem. Soc.* **68** (1946) pp. 599-605.

Since air is an impurity likely to be present in the course of isomerization reactions, the effect of small amounts of oxygen upon the course of isomerization of butanes and pentanes was investigated. The catalyst used for the reaction was aluminum chloride or aluminum bromide. It was found that n-pentane does not undergo isomerization when agitated at 25°C. for 257 hours with aluminum chloride deposited on charcoal. However, in the presence of 0.013 mole percent of oxygen, 93 percent of the pentane was isomerized after 96 hours of agitation, resulting in the formation of isobutane, isopentane and higher-boiling hydrocarbons. It was also found that the addition of 0.007 mole percent oxygen, in the form of air, to n-pentane, is sufficient to convert 40 percent of the n-pentane to butanes and isopentane using aluminum chloride catalyst; in the absence of oxygen the reaction did not proceed. The catalytic effect of an aluminum bromide-oxygen-hydrocarbon complex formed by the action of air upon the solution of aluminum bromide in n-butane was studied. The action of oxygen upon aluminum bromide was investigated. The effect of ethylaluminum dibromide and of diethylaluminum bromide in the presence and in the absence of air upon the isomerization of n-butane was investigated. The mechanism of the isomerization reaction is briefly considered and discussed.

The Catalytic Cyclization of Aliphatic Hydrocarbons. E. F. G. HERINGTON AND E. K. RIDEAL. *Proc. Roy. Soc.* (London) **A184** (1945) pp. 434-46 and 447-63.

The aromatization of a paraffin hydrocarbon proceeds through the formation of a monoolefin which is held on the catalyst by two-point contact. The promoter action of the central atoms in heteropoly acids of molybdenum can be attributed to the stabilization of the molybdenum oxide produced during the hydrogen pretreatment. The alumina used as a support for molybdenum catalysts plays the same role. The variation in yield of the total aromatic hydrocarbon with different paraffin feeds can be calculated by assuming two-point contact. The loss of activity of the catalyst with use is a result of the polymerization to giant molecules of the hydrocarbons adsorbed on adjacent catalyst centers. This loss of activity can be decreased by decreasing the concentration of active centers on the surface. Initial activities for several catalysts are given. The products of catalytic cyclization are discussed. The variation in yield of pentane, hexane, 2-methylpentane, heptane, 2-methylhexane, octane, 3-methylheptane, 2,5-dimethylhexane, 2,2,4-trimethylpentane, nonane are considered. Several hydrocarbons can form aromatics by direct ring closure, as for example, hexane, heptane, 2-methylhexane, octane, 2,5-dimethyl-

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hexane and nonane. Two different types of isomerization to aromatics have been demonstrated. One is exemplified by the formation of p- and m-xylene from octane. This isomerization accompanies ring closure and proceeds smoothly at 475°C. It entails formation and rupture of a subsidiary ring. The results of the passage of many hydrocarbons over an aluminum oxide-supported chromium oxide catalyst at 475°C. are given. Naphthalene is formed when butylbenzene is passed over an aromatizing catalyst. Observed and calculated products are given for a number of hydrocarbons.

Reactions of Aliphatic Hydrocarbons with Sulfur. H. E. RASMUSSEN, R. C. HANSFORD AND A. N. SACHANEN. *Ind. & Eng. Chem.* **38** (1946) pp. 376-82.

The reaction between sulfur and hydrocarbons may be compared to that of oxygen and the hydrocarbons except that sulfur is milder in its reaction than oxygen, and hence more controllable. The paper describes a method for controlling the reaction between sulfur and such hydrocarbons as butane, pentane and hexane to give the corresponding olefins, diolefins, and thiophene or alkylthiophenes. If the charging stock is commercial (95 percent) n-butane, the following variations of the process are possible: (a) an 80 percent conversion to a product consisting of 35 percent thiophene, 35 percent butadiene, and 30 percent n-butylene by weight by recycling unreacted butane; (b) a 75 percent conversion to equal weights of thiophene and butadiene by recycling unreacted butane and butylene; or (c) a 50 percent conversion to thiophene alone by recycling unreacted butane, butylene, and butadiene. Data are presented in some detail in tabular and graphical form.

Ethylation of Benzene in Presence of Solid Phosphoric Acid. V. N. IPATIEFF AND L. SCHMERLING. *Ind. & Eng. Chem.* **38** (1946) pp. 400-402.

Phosphoric acid on kieselguhr, or the so-called solid phosphoric acid, is a good catalyst for the alkylation of benzene with ethylene in continuous operation. The yield of ethylbenzene increases with increase in temperature and pressure; 80 percent conversion of ethylene in a single pass is obtained at about 325°C. and 600 psi or at 280°C. and 900 psi. These results are obtained at a benzene space velocity of 2 cc. per hour per cc. of catalyst. The ratio of monoethylbenzene to polyethylbenzenes increases with increase in benzene-ethylene ratio. It is thus possible to obtain an alykylation product, over 90 percent of which is the desired styrene intermediate. The life of the catalyst is found to be satisfactory. The data secured in the course of the investigation are presented in some detail in two tables and two figures.

The Reaction of Propylene Oxide with Alcohols. H. C. CHITWOOD AND B. T. FREURE. *Jour. Amer. Chem. Soc.* **68** (1946) pp. 680-83.

Base-catalyzed alcoholysis of propylene oxide yields almost exclusively the primary monoethers of propylene glycol. Non-catalytic or acid-catalyzed alcoholysis of propylene oxide yields mixtures of the isomeric ethers. The isomeric ethyl, isopropyl, butyl and 2-ethylhexyl monoethers of propylene glycol were prepared and characterized. 1-Ethoxy-2-propanol was also prepared from 1-chloro-2-propanol and sodium ethoxide, and from propylene glycol and diethyl sulfate. The monoethyl ethers were distinguished by the selective cleavage of the secondary ether group with sulfuric acid and acetic anhydride.

Manufacture: Processes and Plant

Multicomponent Tray Calculations. E. G. SCHEIBEL. *Ind. & Eng. Chem.* **38** (1946) pp. 397-99.

A graphical method is presented for tray calculations for multicomponent systems. The method is based on the use of a pseudo reflux ratio that gives the same number of trays for the binary system of the key components as the actual multicomponent calculations. This pseudo reflux ratio is calculated from a general correlation of the results of a large number of tray calculations. The method is simpler to apply than previous methods in that it requires only the equilibrium curve for the key components. The graphical tray calculations are made by the McCabe-Thiele method. The total trays as determined by this method agree with the rigorous tray calculations to an accuracy of about 5 percent, and the feed tray is located with an accuracy satisfactory for all practical purposes. The results of several typical calculations are presented in tabular form.

Averaging Liquid-Level Control. J. G. ZIEGLER. *Ind. & Eng. Chem.* **38** (1946) pp. 360-64.

Averaging liquid-level controllers are of two types—the simple proportional response type and the proportional plus reset type. The results obtainable with each and the optimum response settings are discussed in the author's paper. A method is presented for determining such factors as the required feed-tank capacity, the type of instrumentation required, and the probable instrument settings for specific, coninuous process installations of averaging liquid-level controls. Equations are given for both types of liquid-level controllers.

Some Fundamental Factors in Choice of Liquid Agitators. I. S. BRUMAGIM. *Chem. & Met. Engr.* **53** (1946) pp. 110-114.

The author discusses propellers and turbines with shrouded and open impellers. Characteristics peculiar to these types of agitators are listed. Mechanics of agitation in the mixing liquid is discussed. The shrouded turbine and the open impeller provide good turbulence and create excellent blending. The shearing action does not become important, however, until the peripheral speed becomes so high as to cause cavitation. The propeller and the radial propeller cause shearing by actual impact of the agitated blade. This is important in the dispersion and the dissolving of solids, particularly where the solids are in sizable lumps. The agitators are consid-

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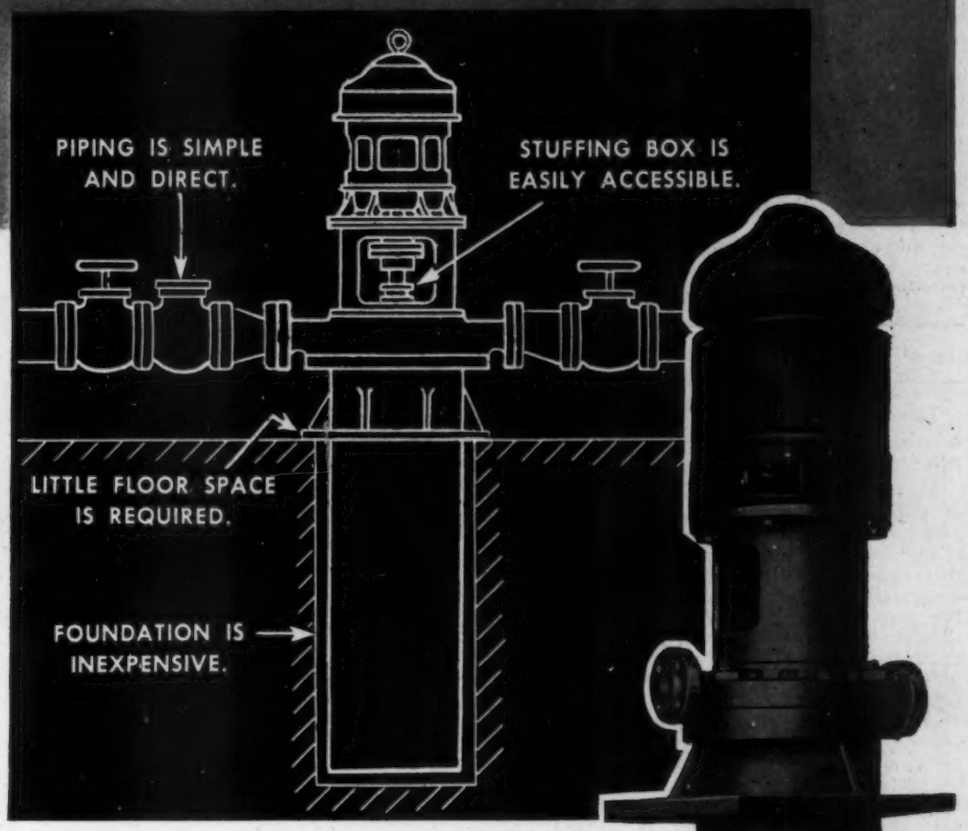
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ered in relation to tanks of different shapes.

Unusual Techniques Feature the Production of Synthetic Bead Catalyst. R. W. PORTER. *Chem. & Met. Engr.* **53** (1946) pp. 94-98.

The synthetic bead catalyst plant of Socony-Vacuum Oil Company at Paulsboro, New Jersey, is described. Catalysts consist of activated alumina contained in silica gel. The important advantage of the synthetic bead over pelleted catalysts lies in its physical ruggedness, its high and sustained activity, its low resistance to vapor flow. When a solution of sodium silicate and an acid are mixed in the right proportions a gel is formed. Into this gel, a catalytic material, activated alumina, is chemically bound. The gel is formed into the desired shape and water is then removed to leave an extremely porous, active and durable material. The finished beads average 3 mm. in diameter, are spheroidal in shape, hard, translucent and consist of approximately 89.5 percent silica, 10 percent aluminum oxide, and 0.5 percent water. The manufacturing process comprises several steps: (1) Preparing the raw materials into the two gel-forming solutions; (2) continuously blending the tow solutions in correct proportions and forming the blend into separate drops of gel, each of which becomes a bead after further treatment; (3) wet heat-treating, base exchanging, and washing the green beads; (4) drying the treated wet beads by reducing their water content to approximately 10 percent; (5) final drying, followed by tempering the dried beads at elevated temperatures; (6) screening, bulk storage, packaging and shipping. Each of these operations is described in some detail. Equipment has been added recently that permits the production of silica gel in these forms. This material has the same advantage in the field of desiccants as the bead has in catalytic operation. A flowsheet of the plant, and pictures of the various parts of it are included at another point in the journal.

Products: Properties and Utilization

The Blending Octane Numbers of 2:5-Dimethylfuran. H. B. NISBET. *Jour. Inst. Petr.* **32** (1946) pp. 162-66.

The author briefly reviews the theory of knocking in a spark-ignition engine and notes that knock is caused by conditions obtaining in the fuel-air mixture just prior to its combustion. Thermal decomposition and partial oxidation of the hydrocarbon molecules give rise to radicals that are chain carriers. These are capable of initiating chain reactions in which the carrier can regenerate itself or may generate a greater number of chain-carrying radicals by the process of chain branching. This chain of reactions can be broken by destruction of carriers by contact with solid surfaces or with other molecules or radicals in the gaseous phase. When the rate of destruction of the chain carriers is greater than the rate of formation, the combustion reaction can be kept within limits, while if the rate of formation exceeds that of destruction, the mixture may inflame spontaneously and the flame speed may be that of a detonating wave, thus causing a knock. In a normal explosion in the cylinder, the spark creates a flame that passes through the fuel-air charge at an almost uniform and fairly low speed. However, in knocking explosions the formation of the chain carriers in the unconsumed fuel-air mixture in front of the flame causes detonation of the latter part of the charge in front of the initial flame. Inductive reasoning suggests that 2:5-dimethylfuran should have high-blending octane numbers in admixture with base fuels of low octane number. The author reports the work done on this subject and notes that the results of engine tests confirm the belief that dimethylfuran should be valuable as a blending agent. A bibliography of 13 references is included. The data secured in the course of the work are presented in 4 tables.

Determination of the Boiling Range of Chlorinated Hydrocarbons. D. WILLIAMS. *Ind. & Eng. Chem., Anal. Ed.* **18** (1946) pp. 157-60.

A study of the factors affecting precision in the determination of distillation temperatures of chlorinated hydrocarbons showed that thermometer calibration errors cause some variation. The rate of distillation was found to be important in some instances. The effect of variations in atmospheric conditions, such as the ambient temperature and drafts, was found to be appreciable. The most important factor was superheating of the vapor. Over limited temperature ranges, distillation temperatures are linear functions of the composition, and it is possible to determine the composition of most binary mixtures and some ternary mixtures by determination of distillation temperature. The apparatus used was essentially that of the A.S.T.M. for determination of the boiling range of gasoline but with some modification of the heater and thermometer. The procedure is described in detail and the data secured are presented in tabular form.

Amperometric Titration of Mercaptans with Silver Nitrate. I. M. KOLTHOFF AND W. E. HARRIS. *Ind. & Eng. Chem., Anal. Ed.* **18** (1946) pp. 161-62.

A rapid and accurate emperometric titration method for the routine determination of primary, secondary, and tertiary mercaptans with silver nitrate is described. A rotating platinum wire electrode was used as the indicator electrode. Amounts of mercaptan sulfur as small as 0.2 mg. in 100 ml. of liquid can be determined with an accuracy of 1 or 2 percent. Larger amounts can be determined with an accuracy and precision of 0.3 percent. The titration requires about 2 minutes. The apparatus and the circuit used are described and shown in the figures, and the procedure is outlined. Typical results of titrations are given in tabular form.

Method for Determining the Instantaneous Hardness of Plastic Substances. A. CAMERON. *Trans. Faraday Soc.* **41** (1945) pp. 583-6.

The method depends upon the use of a weighted cone (40-182 g.) which is dropped from various heights (5 to 35 cm.) onto the surface of the plastic material. A soda grease of an Institute of Petroleum Technologists penetration No.

"Credit for this performance is ascribed by the refinery operators . . . to the faultless performance of the internal gas handling equipment which handled the gas produced. Any fault in the operation of the gas equipment, on which the catalytic cracking unit is wholly dependent, would have interrupted the operation of the Thermofor unit," World Petroleum reported.

This is another of the numerous vapor recovery plants designed and constructed by Petroleum Engineering, Inc., during its 16 years continuous service to the industry. PETROLEUM ENGINEERING, INC. Offices: Houston and Tulsa.

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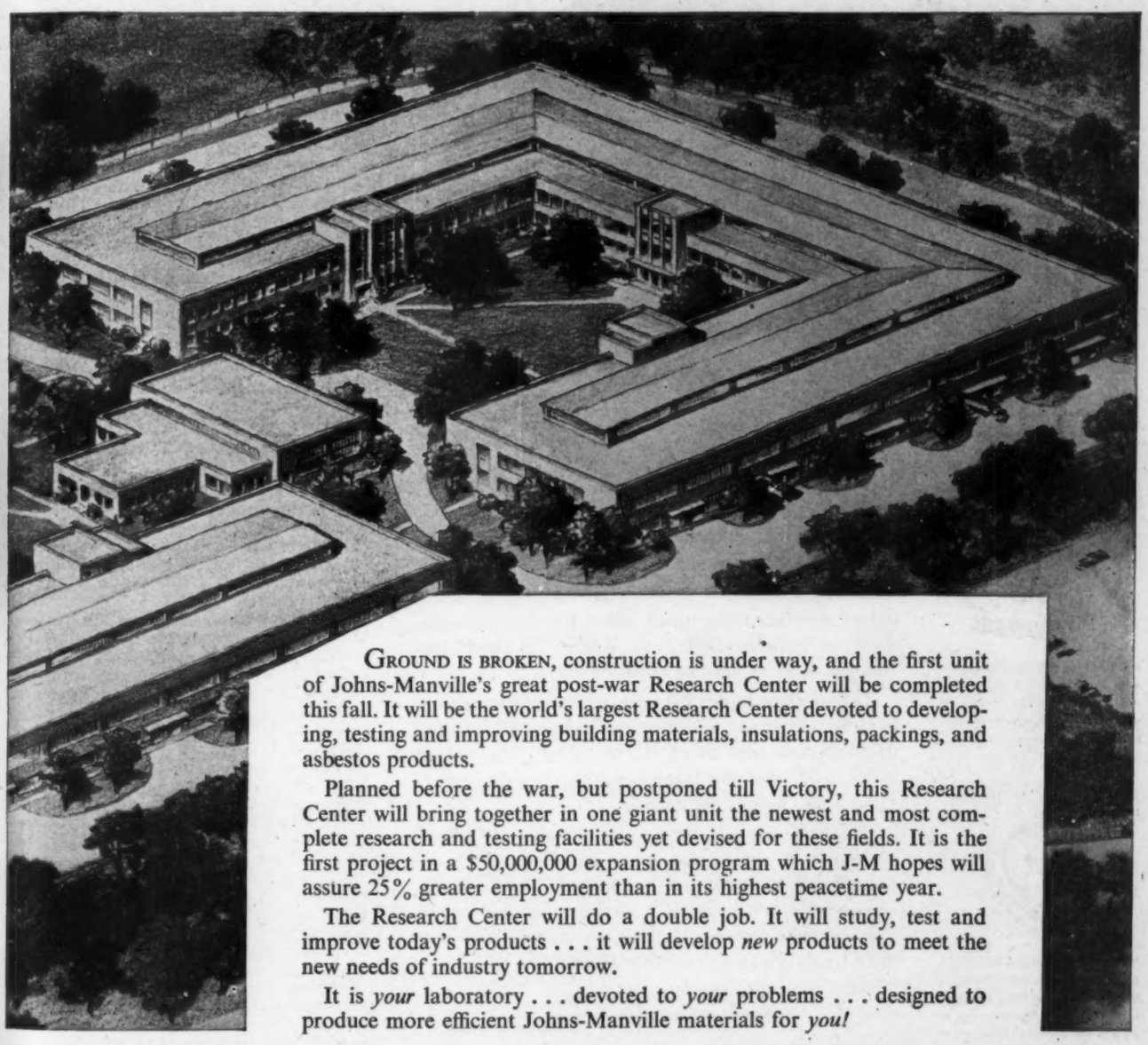

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230 and a lime-grease of 85 penetration number were used in the study. The hardness is given by the energy of impact divided by the volume displaced, which quantity has the dimensions of a stress. This is shown to be substantially independent of the height of drop and weight of the cone. The determination is practically instantaneous, within Maxwell's relaxation time, and, therefore, errors caused by the plastic flow of the system are avoided.

Book Review

Encyclopedia of Hydrocarbon Compounds

Compiled by Joseph E. Faraday, Ph. D. Published by The Chemical Publishing Company, Brooklyn, New York. Volume 1, loose-leaf binder; price $15.00.

This Encyclopedia of Hydrocarbon Compounds is designed to simplify and expedite literary research in the case of hydrocarbon compounds. It presents the following information: molecular formula, structural formula, occurence in nature, names of the compounds, methods of preparation, physical constants, methods of detection and determination, and outstanding properties and reactions. The first volume deals with hydrocarbons containing one to five carbon atoms. The publisher proposes annual new sheets to be inserted in the loose-leaf binder to keep it up to date.

Hydrofluoric Acid Alkylation

Phillips Petroleum Company, Chemical Products Department, Bartlesville, Oklahoma. Cloth, 380 pages; Price $7.50.

This book describes in detail the HF Alkylation process for the manufacture of aviation gasoline. It also describes the equipment used and operating experience gained during the wartime development of commercial HF Alkylation in the oil industry.

The first commercial hydrofluoric acid alkylation unit was built by Phillips Petroleum Company at its Borger, Texas refinery, and placed in operation on December 25, 1942. Because of the war emergency, a meeting was sponsored by the Company at Amarillo and Borger, Texas, February 7 to 12, 1943, to place details on design and operation of the new process before the industry. This meeting was widely attended by refiners and engineering contractors and resulted in requests that the industry be kept advised of developments regarding corrosion rates, mechanical problems, and operations. Phillips supplied this information as a part of its contribution to the war effort, issuing a series of reports to a restricted group of actual HF Alkylation plant operators, covering not only operating experience at Borger but also subsequent commercial operations at its Kansas City refinery, pilot plant, research, and metallurgical investigations, and additional information obtained at Champlin Refining Company, End, Oklahoma, where an HF Alkylation unit, one of the earliest operated by smaller refineries, was started in April, 1944.

With wartime secrecy requirements lifted, the present book is based on these reports which have been revised and brought up to date and compiled into a single volume on HF Alkylation. The original policy used in the reports, the presentation of complete details of the

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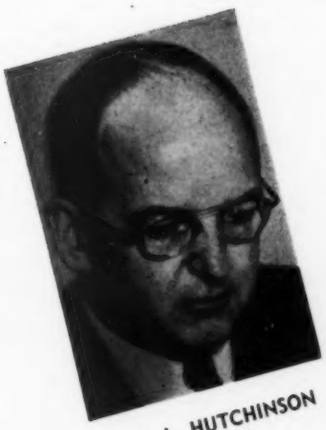

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process, laboratory analyses, equipment operation, etc., has been retained.

Chapter headings in the book are: 1. Chemistry of HF Alkylation; 2. Design of HF Alkylation units; 3. Operation of HF Alkylation units; 4. Correlation of operating variables; 5. Test operations with thermal feeds; 6. Continuous pilot plant alkylation of isobutane with mixed butylenes and amylenes and with propylene; 7. Analytical methods specifically applicable to hydrofluoric acid alkylation; 8. Safety; 9. Properties of hydrofluoric acid; 10. Metallurgy, corrosion, and materials of construction; 11. Operation of Champlin alkylation unit, and 12. Alkylation of catalytic isobutylene-butylene co-polymer. Appendix.

The volume is well illustrated with numerous photographs, equipment diagrams, flow sheets, charts of operating variables, and data on physical properties of hydrocarbons and the hydrofluoric acid catalyst.

In summary, this book reflects a thorough and conscientious effort to present the pertinent information on HF Alkylation to the industry at large, and should be of real value to all engineers, operators, maintenance men, and executives concerned with this process.

New Company Acquires J. A. Abercrombie Stock

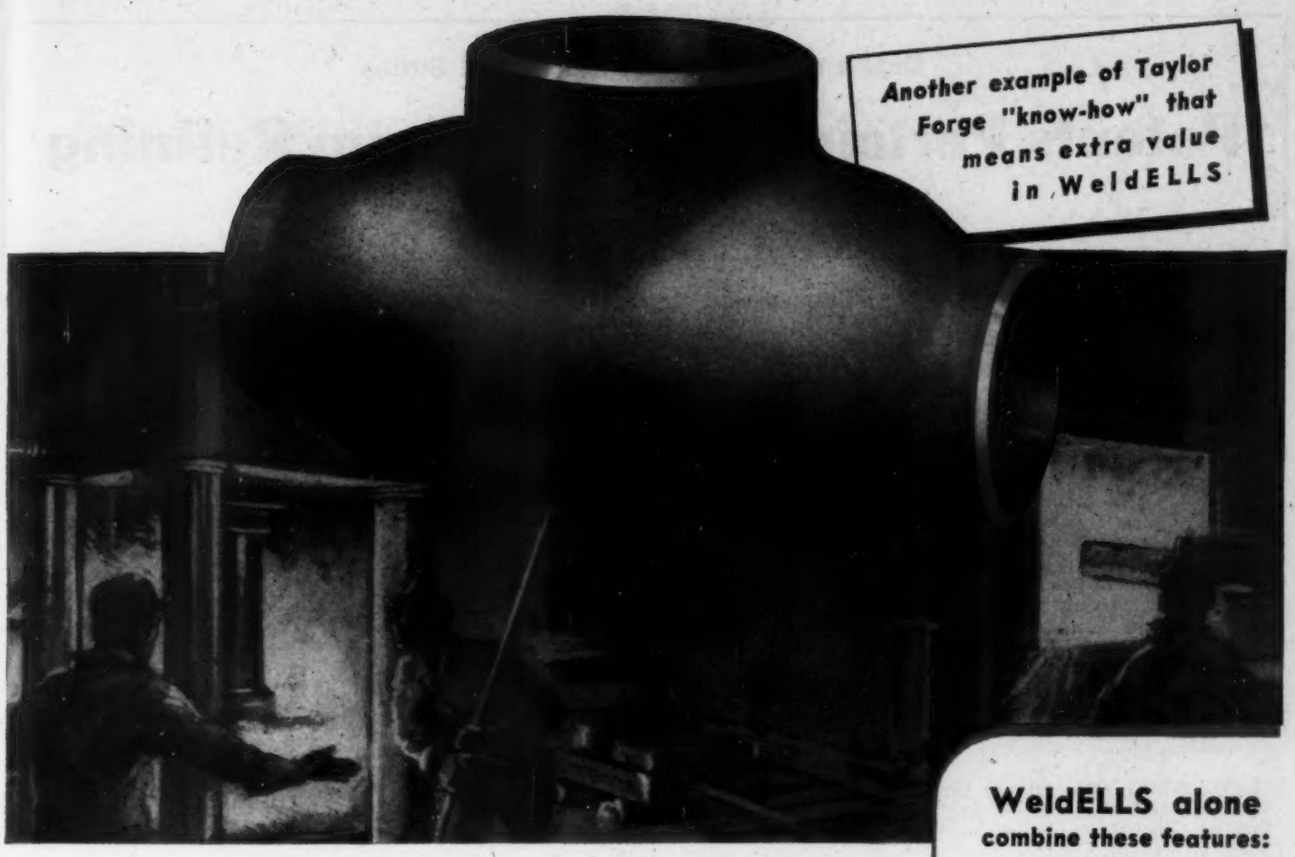
Old Ocean Oil Company has acquired the capital stock of J. S. Abercrombie Company, Houston, for a cash consideration said to be in excess of $50,000,000. Financing was by borrowing from New York banks and a substantial issue of 20-year debentures placed with Stanolind Oil & Gas Company. J. S. Abercrombie Company is one of the principal owners of the Old Ocean field in Brazoria County, Texas, one of the highest rated reserves in the Upper Gulf Coast, and also has holdings at Conroe, in East Texas and in South Louisiana, the whole including 14,500 barrels of current daily production. It jointly owns and operates with Magnolia Petroleum Company a large cycling and gasoline extraction plant in the Old Ocean field.

Stockholders of Old Ocean Oil Company, newly organized with a Delaware charter, include Lloyd Noble of Noble Drilling Company, Ardmore, Oklahoma; Carlton R. Winn of Dallas, an attorney for Stanolind Oil & Gas Company, and Harry C. Weeks of Fort Worth. Winn is president and Noble is vice president. J. R. Butler of the Cotton Valley Operators Committee has been named vice president and general manager. These officers and J. L. Cleveland, president of Guaranty Trust Company of New York are the board of directors. The company will maintain headquarters at Houston.

Old Ocean field was developed originally by J. S. Abercrombie and Harrison Oil Company, the latter's interest having been acquired by Magnolia Petroleum Company.

The Texas Company Plans Philadelphia Refinery

The Texas Company has acquired a 1368-acre site on the Delaware River opposite the Philadelphia Navy Yard, where it plans erecting a refinery, the first unit to be in operation some time in 1948. Details as to type of construction and capacity were not released, and it was indicated progress will be determined by availability of materials.



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Digest of Recently Issued United States

Patents Pertaining to Petroleum Refining

Compiled by HEINZ HEINEMANN

REFINING

U.S.P. 2,397,224. Treatment of Hydrocarbons. D. C. Walsh, Jr., and E. Q. Camp to Standard Oil Development Company.

The object of the invention is to provide a process whereby hydrocarbon reaction product from an alkylation and isomerization process employing $AlCl_3$ and H_2SO_4 catalysts, respectively, may be treated with an alkaline reagent and distilled without causing corrosion of the equipment. Product from the isomerization stage is admixed with a solution of an alkali metal hydroxide and alkylated product added to the mixture. The resulting mixture is treated with additional amounts of a solution of alkali metal hydroxide. After settling, the hydrocarbon phase is distilled.

U.S.P. 2,397,377. Mineral Oil Composition and Method of Suppressing Foaming in Oils. H. G. Smith and T. L. Cantrell to Gulf Oil Corporation.

A mineral oil composition resistant to foaming is described which comprises mineral oil and between 0.01 and 1.0 percent by weight of dimethylaniline isoamyl octyl orthophosphate exhibiting a pH value of between approximately 2 and 4.

U.S.P. 2,397,580. Recovery of Valuable Hydrocarbons. A. L. Ward to The United Gas Improvement Company.

A mixture of isoprene, piperylene and cyclopentadiene is subjected to elevated pressure and temperature in the substantial absence of oxygen to selectively dimerize the cyclopentadiene. This is followed by distillation to separate the monomeric material which may be retreated to remove any significant quantity of residual cyclopentadiene. The monomeric mixture, free from cyclopentadiene, is subjected to fractional distillation to separate isoprene and piperylene from each other.

U.S.P. 2,397,601. Purifying Dicylopentadiene. H. L. Gerhart and L. M. Adams to Pittsburgh Plate Glass Company.

A resinous product is prepared by heating in a closed system a mixture of trimer, tetramer and pentamer of cyclopentadiene dissolved in an unsaturated glyceride oil and in the absence of polymerization catalysts to a temperature within the range of 160-280°C. until a copolymer soluble in petroleum naphtha is obtained.

U.S.P. 2,397,760. Recovery of Hydrogen Halide. A. J. Shmidl to Standard Oil Development Company.

Hydrogen halide is removed from admixture with other gases by contact with a suspension of an anhydrous metal salt of high absorptive capacity for hydrogen halide (such as copper sulfate) supported on a light carrier (such as clay or vermiculite) in an anhydrous organic liquid inert to hydrogen halide (such as paraffinic oil).

U.S.P. 2,397,768. 2,397,769. Recovery of Hydrogen Halides from Gases. E. F. Wadley to Standard Oil Development Company.

Gases containing hydrogen halide are contacted with a slurry of anhydrous copper sulfate in a paraffinic type hydrocarbon. An amount of 25 percent by weight of anhydrous copper sulfate based on the hydrocarbon employed is preferably used. The process is carried out in two stages, absorption taking place at 60-100°F. at atmospheric pressure, desorption at 325-380°F.

U.S.P. 2,397,839. Process for the Recovery of Toluene. Charles R. Clark to Allied Chemical and Dye Corporation.

A process for the recovery of toluene is described which comprises distilling an oil fraction containing toluene and like-boiling, non-aromatic hydrocarbons which boils within the range 95-118°C. and rectifying the distilled vapors having an endpoint of 111°C. in the presence of a quantity of p-dioxane which selectively carries over as distillate with p-dioxane the toluene like-boiling non-aromatic hydrocarbons and leaves a hydrocarbon residue enriched in toluene.

U.S.P. 2,398,101. Separation of Hydrocarbons. M. R. Lipkin to Sun Oil Company.

Aromatic hydrocarbons are recovered from a liquid hydrocarbon mixture containing the same and boiling in the gasoline or kerosine range, by treating the mixture with an adsorbent conforming substantially to silica gel in adsorbing properties. The adsorbed aromatics are removed from the adsorbent and the adsorbent is regenerated by washing it with a non-aromatic liquid hydrocarbon material of low adsorptive capacity.

U.S.P. 2,398,281. Antiknock Agent. E. Bartholomew to Ethyl Corporation.

The invention relates to the use of halides together with lead antiknock compounds. The halides inhibit the decomposition of lead compounds in the engine. The corrective agent proposed contains bromine and chlorine with the chlorine predominating. A good agent is prepared by admixing on a volume basis 404 parts of ehtylene dichloride and 220 parts ethylene dibromide with 1000 parts tetraethyl lead.

U.S.P. 2,398,282. Antiknock Agent. E. Bartholomew to Ethyl Corporation.

An antiknock mixture is described which consists of 3 parts by volume of iron pentacarbonyl and 1 part of tetraethyl lead.

U.S.P. 2,398,197. Ketones in Aviation Gasoline. A. L. Stanly to Shell Development Company.

Aviation gasoline antiknock agents are described which consist of about 0.25-1 percent of aniline and between 3 and 5 percent of an asymetric ketone selected from the group consisting of the 5 and 6 atom dialkyl ketones.

U.S.P. 2,398,301. Removal of Highly Unsaturated Hydrocarbon Impurities from Diolefin-Containing Mixtures. L. K. Frevel to The Dow Chemical Company.

A vapor mixture containing a conjugated diolefin as the principal hydrocarbon ingredient and containing as an impurity a minor amount of a different and at least equally unsaturated hydrocarbon is passed in contact with a finely divided substance consisting of copper, iron or their oxides at a reaction temperature below 375°C. The impurity is largely destroyed, leaving the conjugated diolefin in a form substantially free of the same.

U.S.P. 2,398,612. Oxidation of Organic Compounds. I. Bergsteinson, J. R. Scheibli and F. H. Dickey to Shell Development Company.

In the oxidation of gaseous organic compounds such as of propane to propinoaldehyde, a higher yield of carbonylic product is obtained in a shorter time by passing the reaction mixture successively through two reaction zones, the second of which is packed with a peroxide-destroying catalyst, such as silicon carbide porous aggregates.

CATALYST PREPARATION ACTIVATION AND REGENERATION

U.S.P. 2,397,505. Catalytic Cracking and Catalyst Reactivation. R. W. Richardson to Standard Oil Development Company.

A cracking process is described which utilizes an acid-treated bentonite, impregnated with an active metal oxide as catalyst. The catalyst is periodically regenerated by oxidation and its activity is maintained at a high level by occasionally subjecting the modified clay to further acid treatment.

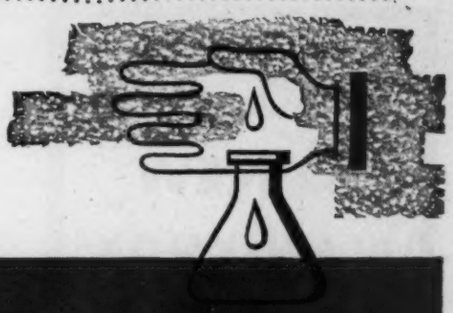
U.S.P. 2,398,175. The Treatment of Sulphide Catalysts. R. M. Cole to Shell Development Company.

Metal sulphide catalysts which have become partially spent due to deposition of carbonaceous material thereon are regenerated by purging with steam to remove hydrogen and hydrocarbons, then adding oxygen to the steam at such a rate that the temperature is maintained between 1200 and 1400°F. After a while hydrogen sulphide is added to the steam at a rate such that the catalyst temperature does not exceed 1400°F. Finally, the catalyst is treated with hydrogen at 700-900°F. under 20 atmospheric pressure.

U.S.P. 2,398,186. Catalyst Regeneration. J. W. Loy to Phillips Petroleum Company.

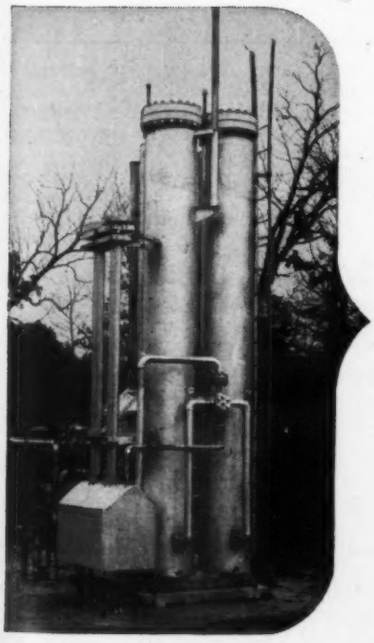
It is an object of the invention to employ the pressure of a diluent gas, such

For effective, economical



DEHYDRATION

OF GASES AND LIQUID HYDROCARBONS



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as steam, to maintain the required pressure in a catalytic process. The steam is passed under pressure through a jetting device and by the aspiratory action of the jetting device, the necessary free-oxygen-containing gas is drawn and then injected into the process, where it supports combustion during the regeneration step.

CRACKING AND REFORMING

U.S.P. 2,397,329. Selective Catalytic Cracking. R. F. Ruthruff.

In the catalytic conversion of a hydrocarbon oil the steps are claimed including heating the raffinate oil obtained from the hydrocarbon oil by solvent extraction ot a relatively low hydrocarbon cracking temperature, contacting the heated raffinate oil with a cracking catalyst for a time sufficient to effect substantial conversion to hydrocarbon conversion products of lower boiling point than said raffinate oil, fractionating the reaction products in a first fractionating zone into gas, the aforementioned liquid hydrocarbon conversion products and cycle stock, admixing said liquid hydrocarbon conversion products with the aforementioned hydrocarbon oil, solvent extracting the mixture and fractionating the raffinate phase in a second fractionating zone into substantially saturated hydrocarbon conversion products and the previously mentioned raffinate oil.

U.S.P. 2,397,485. Chemical Process. C. E. Hemminger to Standard Oil Development Company.

Hydrocarbons are cracked in a process comprising vaporizing the hydrocarbon oil, conducting the vapors to a zone containing a dense suspension of powdered inert material, which powdered material is at higher temperature than the entering vapors, separating the major portion of the inert material from the oil vapors and conducting the oil vapors to a reaction zone where they contact a catalyst adapted to effect the desired conversion.

U.S.P. 2,397,638. Conversion of Hydrocarbons. R. T. Bell, H. O. Folkins and C. M. Thacker to The Pure Oil Company.

To facilitate the cracking of hydrocarbons, a small amount of hydrogen halide and a small amount of ozone, air, oxygen or other free-oxygen-containing gas is mixed with the hydrocarbons subjected to decomposition. Proportions range from 0.25-5 mol percent of hydrogen halide and 0.25-5 mol percent of oxygen based on the mixture. An amount of free-oxygen-containing gas sufficient to oxidize the hydrogen halide to water and free halogen gives good results.

U.S.P. 2,398,228. Starting Procedure for Cracking Units. E. W. Hunt to Standard Oil Development Company.

A fluid-flow catalytic-cracking operation of the down-flow type is started by setting the catalyst into motion with a hot gas. After the temperature of the catalyst cycle has substantially increased, a small amount of oil having heavy constituents and lighter constituents is injected into the reactor. The heavy constituents are deposited on the catalyst and burned in the regenerator, increasing the temperature of the catalyst. This procedure is continued until the temperature of the catalyst has reached process operating temperature.

U.S.P. 2,398,280. Cracking of Hydrocarbon Oils. J. M. Barron to The Texas Company.

Oil is vaporized and delivered to the lower portion of a catalytic reaction zone into the upper portion of which a high-boiling liquid containing suspended catalyst is introduced so that the upwardly rising vapors are contacted with dispersed or suspended catalyst and refluxed with high-boiling liquid. Liquid-containing catalyst and vapors are separately withdrawn.

U.S.P. 2,398,489. Catalytic Conversion Process. M. H. Arveson to Standard Oil Company (Indiana).

A catalytic cracking process is described according to which spent catalyst is transferred in a dense aerated condition to the regeneration zone and regenerated catalyst is transferred to the reaction zone in a slurry with the hydrocarbon feed. The process provides a long catalyst residence time and a low catalyst-to-oil ratio. Hydrocarbon oil is heated and vaporized in the presence of the catalyst.

U.S.P. 2,398,739. Catalytic Cracking Process. B. S. Greensfelder and S. Z. Perry to Shell Development Company.

Hydrocarbon oils boiling above 311°F. are preheated to 700-825°F., combined with a mixture of air and a hot regenerated catalyst consisting of a finely divided adsorptive silica-alumina-zirconia composite diluted with a finely divided substantially non-adsorptive and non-combustible mineral diluent and cracked at a temperature in the range of 1200-1400°F. An hourly space velocity of 6-10 is observed. Cracked products rich in normally gaseous olefins are separated from the catalyst which is regenerated with air at 1200-1400°F. and at a temperature about 50°F. higher than the cracking temperature.

ISOMERIZATION

U.S.P. 2,397,639. Catalytic Isomerization of Olefinic Hydrocarbons. L. Berg, G. L. Summer, Jr., and C. W. Montgomery to Gulf Research & Development Company.

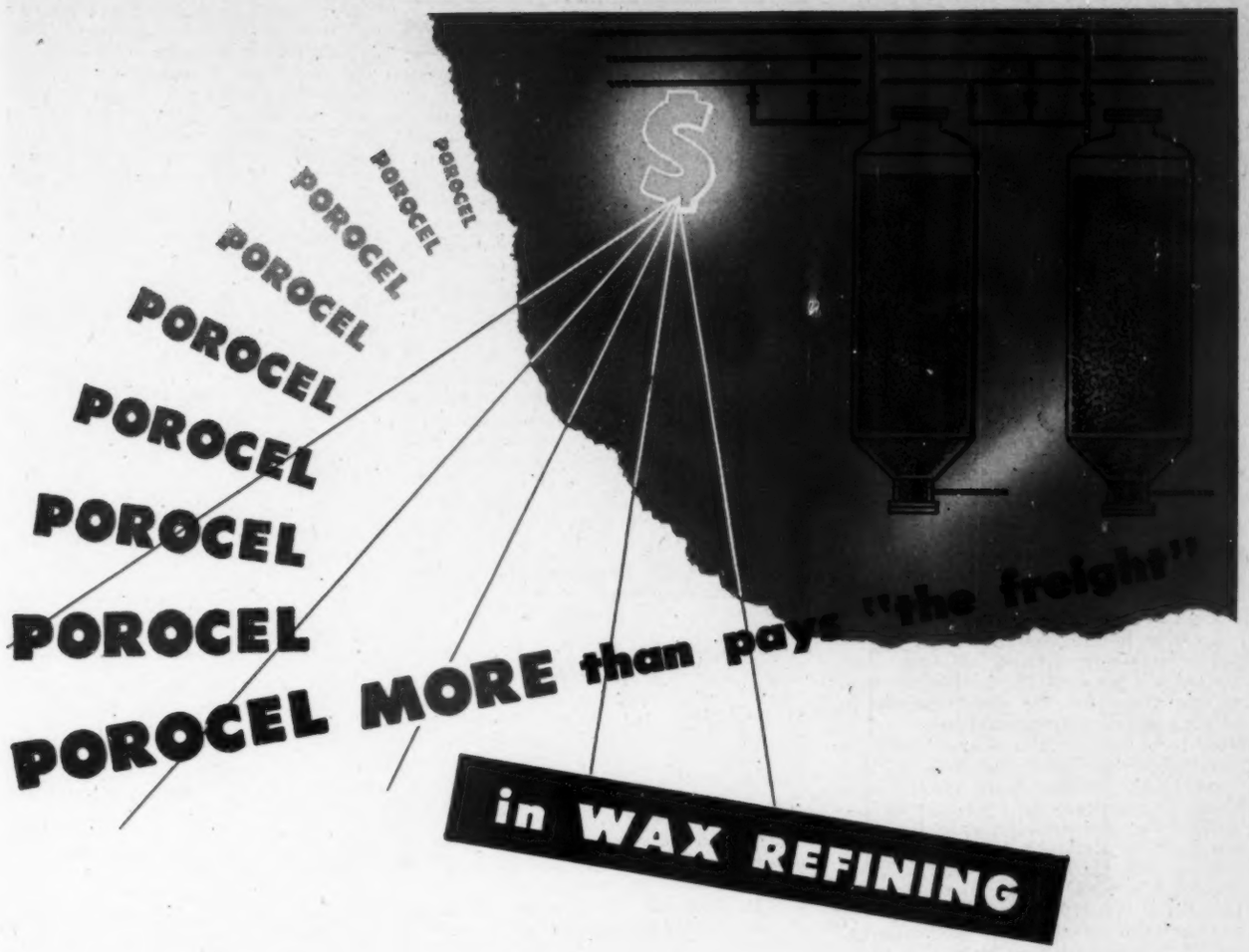
Gasoline or naphtha containing an appreciable quantity of olefins is passed over a catalyst of alumina, impregnated with anhydrous HCl. Reaction conditions of 300-600°C., a space velocity of 0.1-20 volumes per volume per hour and pressures of 0-200 psi are employed. The octane rating of the charge is increased due to isomerization of the olefins.

U.S.P. 2,397,820. Treatment of Hydrocarbons. R. B. Thompson and J. A. Chenicek to Universal Oil Products Company.

Normal-butane is isomerized in the presence of $AlCl_3$ and a catalyst promoter comprising an ethyl chloride-normal-butane azeotrope formed during a subsequent alkylation step in which isobutane, a HCl-containing fraction and ethylene are reacted in the presence of an $AlCl_3$ catalyst.

U.S.P. 2,397,925. Conversion of Paraffin Hydrocarbons. P. L. Cramer and C. R. Begeman to General Motors Corporation.

The isomerization of paraffin hydrocarbons with an aluminum halide catalyst is carried out in the presence of a nitroparaffin as promoter. The promoter



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is used in amounts of 0.5 to 4 mol percent of the reaction mixture.

U.S.P. 2,398,563. Process for Preparing Branch-Chain Hydrocarbons. W. R. Smith and A. R. Goldsby to The Texas Company.

The isomerization of relatively low boiling hydrocarbons such as n-pentane in the presence of a liquid aluminum chloride-hydrocarbon complex catalyst is advantageously carried out in the presence of from 0.1-0.6 percent of an aromatic hydrocarbon which reduces cracking and other side reactions. Most of the aromatic hydrocarbon is dissolved in the catalyst complex, which is occasionally withdrawn and treated with olefins to alkylate dissolved aromatic hydrocarbons. Alkylated products are removed and catalyst complex is returned to the isomerization zone.

ALKYLATION

U.S.P. 2,397,085. Manufacture of Motor Fuel. E. R. Boedecker and A. G. Oblad to Socony-Vacuum Oil Company.

High-octane gasoline is produced in a process including an alykylation step, a defluorination step, and an isomerization step. The contact materials are used in one stage for the defluorination of alkylate-product hydrocarbons, and in another stage, for the isomerization of terminal-bond olefins contained in alkylation charge stocks. After use the catalysts are regenerated for further utilization in the process. Separate beds are provided for defluorination and isomerization and the flow is alternated at regulated intervals. Regeneration is carried out at 900-1100°F. with an oxidizing gas. Suitable catalysts are e.g. alumina gel or dehydrated bauxite.

U.S.P. 2,397,495. Conversion of Alkylated Aromatic Hydrocarbons. A. P. Lien and B. H. Shoemaker to Standard Oil Company (Indiana).

Ethylbenzene is produced from an alkyl benzene containing at least three C atoms in the alkyl group (such as isopropyl-benzene) by contacting the alkyl benzene with a catalyst of HF promoted by 2-20 weight percent of BF_3 at 150-400°F. and under sufficient pressure to maintain liquid phase.

U.S.P. 2,397,542. Alkylation. A. W. Francis and E. E. Reid to Socony-Vacuum Oil Company.

The yield of alkyl benzene obtained in the treatment of benzene with olefins in the presence of $AlCl_3$ or other Friedel-Crafts type catalysts can be greatly increased by conducting the reaction at 100-150°C. and under 100-300 psi pressure. The catalyst is used in amounts of from 0.02-0.1 mol per mol of benzene.

U.S.P. 2,398,495. Alkylation. E. d'Ouville and B. H. Shoemaker to Standard Oil Company (Indiana).

Polymers of normal olefins which are relatively viscous or of relatively high molecular weight are comingled with an excess of a paraffinic or naphtenic hydrocarbon affording at least one tertiary C-atom in the presence of alkylation catalysts (such as active halide or acidic catalysts) at 30-150°F. viscous, substantially saturated hydrocarbon oil boiling substantially above the boiling range of gasoline and having a viscosity of at least 500 seconds Universal at 100°F. are produced.

POLYMERIZATION, CONVERSION

U.S.P. 2,397,301. Chemical Process. H. G. Vesterdal to Standard Oil Development Company.

Propylene is converted to its dimer and trimer by subjecting it at 775-800° F. and under 2100-2400 psi pressure to the action of a chromium oxide catalyst supported on alumina. The reaction is carried out in the presence of between 0.25 and 5 mol percent of steam.

U.S.P. 2,397,945. Polymerization of Propylene. D. E. Burney, E. L. d'Ouville and C. M. Hull to Standard Oil Company (Indiana).

Synthetic lubricating oil of high thermal stability is produced by polymerizing a liquid propylene-containing hydrocarbon stream in the presence of a fluid $AlCl_3$ catalyst dispersed in a hydrocarbon oil. The reaction is carried out under sufficient pressure to prevent vaporization and at a temperature of 30-200° F.

U.S.P. 2,398,462. Processes for Catalytic Benzene Synthesis. O. Roelen and W. Feisst to The Alien Property Custodian.

A mixture of CO and hydrogen is passed at synthesis temperature over a carrier catalyst which has been obtained by pretreating the carrier material with acids to remove soluble constituents and combining, while avoiding a strongly alkaline reaction, the acid-treated carrier material with iron group metal compounds precipitated from salt solutions with alkaline precipitants. Normally liquid hydrocarbons are separated from the reaction products.

U.S.P. 2,398,468. Process for the Treatment of Hydrocarbons. W. A. Schulze and G. H. Short to Phillips Petroleum Company.

The polymerization of substantially pure butadiene under storage conditions is prevented by the addition of from 0.001 to 1.0 percent by weight of an inhibitor consisting of ammonia. The inhibitor is removed prior to polymerization of the butadiene by intimate contact with an aqueous acid solution.

U.S.P. 2,398,496. Hydrocarbon Conversion and Fractionation System. W. C. Edminster and D. H. Pollock to Standard Oil Company (Indiana).

A hydrocarbon conversion and fractionating process is claimed comprising heating a hydrocarbon fluid in a heating zone to increase its temperature, introducing into the fluid at a mixing zone a catalyst in a continuous uninterrupted flow at an effective pressure above the pressure of the fluid and passing catalyst from the mixing zone to a reaction zone and the hydrocarbon product therefrom to a fractionating zone and by-passing the fluid around the mixing zone and reacting zone to the fractionating zone when the effective pressure of the catalyst is less than a predetermined minimum.

HYDROGENATION, DEHYDROGENATION, AROMATIZATION

U.S.P. 2,397,218. Conversion of Hydrocarbons. J. F. Sturgeon to Universal Oil Products Company.

The invention comprises a process for dehydrogenating aliphatic hydrocarbons in the presence of a catalyst formed by precipitating an alumina hydrogel by the addition of a base to an aqueous solution of an aluminum salt, sufficiently freezing and then thawing the hydrogel to destroy its gelatinous structure and convert it into a substantially amorphous and non-gelatinous powder and an aqueous solution, removing a major proportion of said aqueous solution from the powder and mixing it with a solution of a metal compound under conditions to impregnate the powder with the oxide of the metal. The composite is then dried, formed and calcined.

U.S.P. 2,397,352. Chemical Process. C. E. Hemminger to Standard Oil Development Company.

To dehydrogenate hydrocarbons, the hydrocarbons and a powdered catalyst are passed into the bottom of a reaction zone whose lower portion is of a more restricted cross-sectional area than its upper portion. The mixture is caused to flow concurrently upward in the reactor. Catalyst is withdrawn from the upper portion of the reactor, regenerated, conducted into a zone containing a reducing gas undergoing combustion to heat the catalyst and returned to the reaction zone at a temperature higher than that of the hydrocarbon introduced simultaneously.

U.S.P. 2,398,074. Process for Manufacturing Toluene. D. G. Brandt to Cities Service Oil Company.

A largely paraffinic petroleum distillate is passed in a confined stream of restricted cross section through a pipestill furnace and cracked at a temperature of about 980° F. The products are immediately and instantly cooled to 600-700° F. The resulting vapor products are fractionated to segregate a distillate boiling between 250 and 500° F. This distillate is passed in a confined stream of restricted cross section through a heating zone in which it is vaporized and super heated to a temperature of from 800-1200° F. and it is then digested in an enlarged zone either with or without contact with a catalyst. The resulting products, rich in toluene are quickly cooled to 600° F. and then fractionated.

U.S.P. 2,398,126. Dehydrogenation of Hydrocarbons. C. M. Thacker and R. T. Bell to The Pure Oil Company.

The catalytic dehydrogenation of hydrocarbons can be accelerated and improved yields can be obtained by carrying out the reaction in the presence of mercury vapor. Between 0.1 and 5 percent mercury vapor by volume of the gases undergoing reaction is added to the hydrocarbon vapors to be dehydrogenated.

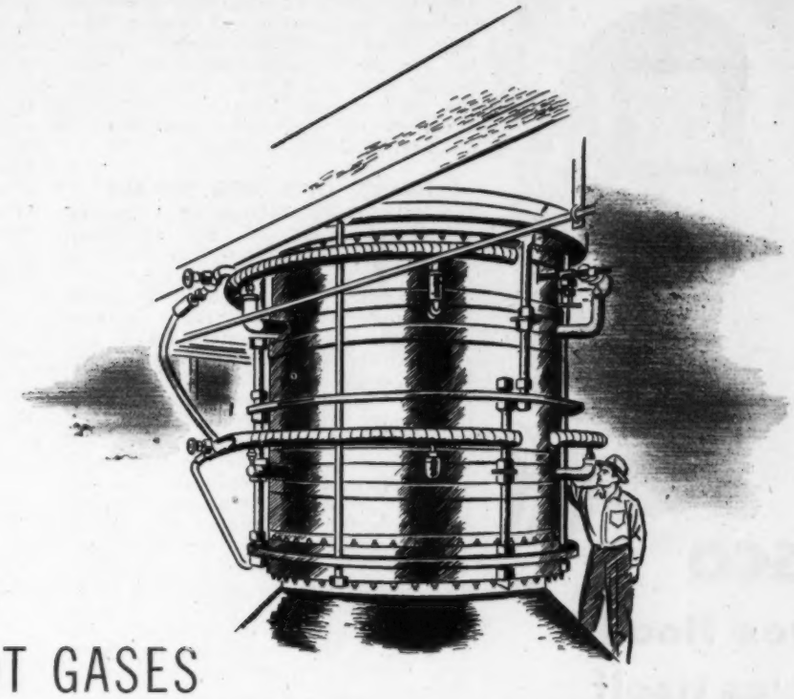
U.S.P. 2,398,674. Hydrocarbon Conversion Process. W. A. Schulze to Phillips Petroleum Company.

A hydrocarbon feed mixture boiling between 150-375° F. and comprising about 28-30 parts olefins, 20-22 parts paraffins, 20-25 parts naphthenes and 20-25 parts aromatics is treated with a bauxite catalyst at 1000-1300° F. and a liquid space velocity of 0.1-10.0. Substantial conversion of non-aromatic to aromatic hydrocarbons occurs. The catalyst can be regenerated at 1400-1500° F.

DESULFURIZATION

U.S.P. 2,397,077. Refining of Mineral Oils. J. C. Alspaugh to Standard Oil Development Company.

The invention is concerned with the removal of sulfur compounds from feed



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oils utilizing a mineral acid such as sulfuric acid. The acid oil after removal of the acid sludge, is contacted with an aqueous solution containing dissolved therein a small amount of calcium chloride. After a sufficient contact period, the calcium chloride-treated oil is removed from the calcium chloride solution and treated with a neutralizing agent which preferably comprises a sodium hydroxide solution.

HEAVY OILS AND WAXES

U.S.P. 2,397,662. Method of Preparing Lubricating Oils. L. M. Henderson and W. G. Annable to The Pure Oil Company.

Lubricating oil is prepared by distilling cylinder stock under light cracking conditions at approximately 700° F. and substantially atmospheric pressure in the presence of a light hydrocarbon diluent, injecting steam into the body of cylinder stock undergoing distillation at such rate that the volume of steam is approximately equal to the volume of hydrocarbon vapor produced. The distillate is contacted until approximately 91.2 percent by volume of the cylinder stock is distilled. Approximately 15 percent petrolatum is added to the distillate and fractions boiling within and below the gasoil range are removed. The remainder is diluted with naphtha, chilled to —35° F. and centrifuged to remove wax. Naphtha is removed from the dewaxed oil.

U.S.P. 2,397,702. Agent for Mineral Oils and Mineral Oil Composition Containing Same. H. G. Smith and T. L. Cantrell to Gulf Oil Corporation.

An additive for mineral oils is described consisting of a calcium salt of a sulfurized derivative of a ricinoleic acid reaction product of a diaryl-chlorophosphite which has been made by esterifying an alkylated phenol which contains at least one alkyl group having from 3-5 C atoms per mol with PCl_3.

U.S.P. 2,397,771. Diesel Fuel Oil. B. T. Anderson and M. T. Flaxman to Union Oil Company of California.

To a diesel fuel having a cetane number of 50-65, but defficient in lubricating properties is added a minor proportion (0.01-0.5 percent) of a high-molecular-weight organic acidic material which will impart lubricating properties thereto. The additive comprises naphthenic acids obtained from petroleum fractions by caustic treatment and recovered as bottoms fraction by distilling over the normally liquid naphthenic acid components.

U.S.P. 2,397,859. Liquid Fuel and Method of Producing Same. A. B. Hersberger and K. M. Thompson to The Atlantic Refining Company.

Coal or other bituminous material is pulverized in the presence of a small amount (0.1-5 percent) of an acidic stabilizing agent such as an organic or inorganic acid or a derivative thereof and the mixture is suspended in hydrocarbon oil. A stable suspension results.

U.S.P. 2,397,868. Two-Stage Deoiling and Dewaxing. V. N. Jenkins to Union Oil Company of California.

In a process for the separation of a mixture comprising lube oil, low-melting wax and high-melting wax, wherein the separation is effected in two stages in which the high-melting wax is separated in the first stage by a dewaxing solvent containing about 90 percent methyl ethyl ketone and 10 percent benzene, and the low-melting wax is separated in the secohd stage by a dewaxing solvent containing about 50 percent methyl ethyl ketone and 50 percent benzene, the step is claimed which comprises fractionally distilling the solvent which is poor in methyl ethyl ketone, in the presence of a sufficient amount of water, whereby two fractions are obtained, one of which consists of methyl ethyl ketone free from benzene and the other of which consists of water and benzene containing about 20 percent of methyl ethyl ketone.

U.S.P. 2,398,193. Lubricant. T. E. Sharp to Standard Oil Company (Indiana).

A rust-preventing lubricating composition comprising about 5 percent of sorbitan mono-oleate, about 5 percent of a soap of a preferentially oil-soluble petroleum sulfonic acid produced by treating a petroleum distillate having a viscosity in the range of about 50-1000 seconds Saybolt Universal at 100° F. with from about 6 to about 9 pounds of strong sulfuric acid per gallon of distillate, and a hydrocarbon lubricating oil.

U.S.P. 2,398,173. Lithium Soap Greases. L. C. Brunstrum and H. J. Liehe to Standard Oil Company (Indiana).

A lithium soap grease is claimed comprising at least 5 percent of a lithium soap, a major proportion of a hydrocarbon oil and between about 0.2 and 2 percent of an unsulfurized ester of a polyhydric alcohol and an acid.

U.S.P. 2,398,415. Mineral Oil Composition and the Like. G. H. Denison, Jr., and P. C. Condit to California Research Corporation.

Higher dialkyl selenides or tellurides, containing at least 8 C atoms in one alkyl group and preferably containing at least 8 C atoms in both alkyl groups are added in small amounts to hydrocarbon lubricating oils. They exhibit effects which are observed with the corresponding dialkyl sulfides only in combination with activators or functional groups.

U.S.P. 2,398,416. Compounded Oil. G. H. Denison, Jr., and P. C. Condit to California Research Corporation.

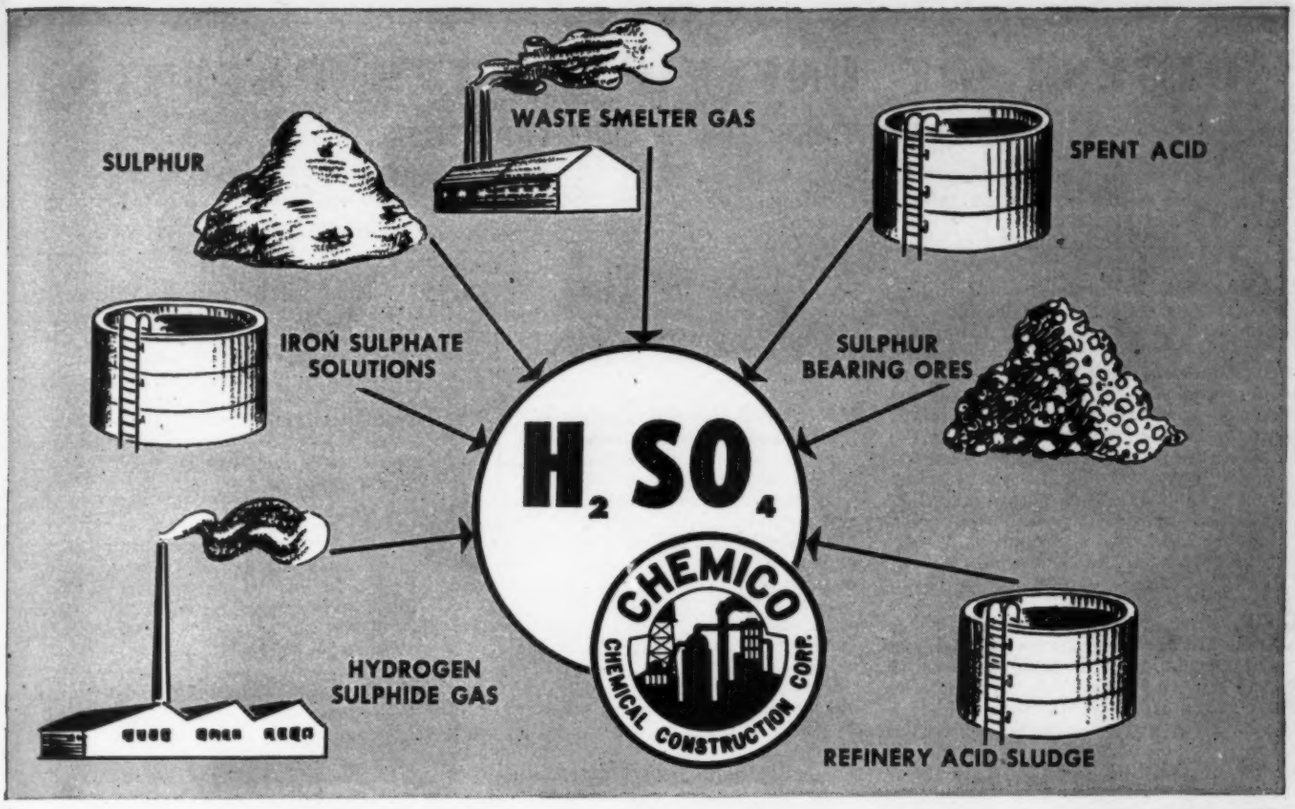
Antioxidants and corrosion inhibitors for lube oils are described which will function in the lube oil in conjunction with metal detergents to provide an oil improved in detergency without increase of corrosiveness and of instability to oxidation. Suitable compounds have the structure.

$$\equiv C - (Se)_m - C \equiv$$

wherein the C atoms are aliphatic C atoms and m is 1 or 2.

Standard Development Gets Award for Flame Thrower

Standard Oil Development Company recently received Naval Ordnance's Certificate for Exceptional Service in recognition of its contribution to development of the Navys' flame thrower and of jellied gasoline which made the weapon more effective and lessened danger to the men operating it. Named with Dr. Robert P. Russell, president of Standard Oil Development Company, as instrumental in developing the flame thrower, were N. F. Myers, H. G. M. Fischer, M. D. Haworth, S. H. Hulse, J. O. Collins, G. W. Engisch, and R. L. Betts, all of the company's laboratories at Bayway, New Jersey.



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DIGEST OF UNITED STATES PATENTS

ON POLYMERIZATION OF HYDROCARBONS

Compiled by HEINZ HEINEMANN

U.S.P. 2,363,221. Polymerization of Hydrocarbons. Lewis A. Bannon to Standard Oil Development Company.

In order to produce a polymerized material with a very high percentage of trimer and small percentages of the dimer or products of higher mol. weight than the trimer, BF_3 gas is used as the catalyst, the time of contact between the gaseous hydrocarbons and the catalyst being very brief. The quantity of BF_3 used is 0.1 to 1 percent and the period of contact less than 1 second at a temperature from atmospheric to about 100-150° C.

U.S.P. 2,363,910. Hydrocarbon Drying Oils. Miller W. Swaney to Standard Oil Development Company.

An alkyl-alpha-acetylene, in which the alkyl group is a methyl, an ethyl, or a higher alkyl group, is subjected to the action of a polymerization catalyst, preferably of the Friedel-Crafts type, at a temperature sufficiently low to maintain the reactant in liquid phase, and preferably at a temperature below —10° C. A good yield of polymerization products is obtained, including a substantial quantity of symmetrically alkylated benzene, and including also a substantial quantity of higher-molecular-weight polymers having the character of lightly alkylated aromatics with unsaturated aliphatic substituent side claims.

U.S.P. 2,366,171. Hydrocarbon Conversion. Arnold Belchetz and Myrle M. Perkins to The M. W. Kellogg Company.

Olefin hydrocarbons are absorbed in a liquid acid at temperatures below polymerizing temperatures, and the solution thus obtained is heated under pressure to a temperature sufficiently high to polymerize the absorbed olefins in the liquid phase. In order to obtain dimers as the main polymerization product, the solution while at the low temperature but under a superatmospheric pressure is mixed with vapors of a hydrocarbon, boiling above the polymerizing temperature at said pressure, in proportions which produce a resulting mixture of solution and condensed vapors which is at the desired polymerizing temperature. After the polymerization has been permitted to proceed to the desired degree, the pressure is lowered to permit vaporization of at least a portion of the condensed hydrocarbon to cool the unvaporized remainder of the reaction mixture to a temperature at which further polymerization is inhibited.

U.S.P. 2,366,325. Polymerization of Dienes. Charles F. Fryling to The B. F. Goodrich Company.

The polymerization of butadiene is carried out in the presence of a free higher fatty acid such as myristic or palmitic acid in order to increase the speed of polymerization, lower the temperature of polymerization, increase the yield of polymer, and improve the quality of polymer. The polymerizing mixture, which may contain another unsaturated organic compound copolymerizable with butadiene, is used in an aqueous emulsion.

U.S.P. 2,367,810. Polymerization of Styrene and its Derivatives. V. H. Turkington and L. R. Whiting to Bakelite Corporation.

Monomeric compounds containing a styrene nucleus are polymerized by heating them in the presence of a two-component catalyst composition the one component of which is a boric acid whereas the other one is oxalic acid or an oxalic acid ester of univalent hydrocarbon radicals. Instead of the boric acids other oxy-compounds of boron may be used wherein each boron atom has at least one of its valences satisfied by linkage with an oxygen atom such as B_2O_3, metallic borates such as $MnH_4(BO_3)_2$, organic borates, alkali borates such as $Na_2B_4O_7$, etc.

U.S.P. 2,368,538. Copolymers of Isoolefins and Diisobutenyl Ring Compounds. A. H. Gleason and W. J. Sparks to Standard Oil Development Company.

A series of new interpolymers of an isoolefin, such as isobutylene with a substituted aryl compound having unsaturation in the substituent radicals such as diisobutenyl benzene is prepared. For this purpose a mixture of 98-20 parts of an isoolefin and 80-20 parts of an aromatic diolefin, eventually diluted by a solvent or the like is cooled to a temperature below —10° C. and then caused to polymerize by the addition of a solution of $AlCl_3$ in an alkyl-halide or other inert low-freezing solvent.

U.S.P. 2,370,010. Method of Polymerization. A. M. Clifford and W. D. Wolfe to Wingfoot Corporation.

A mixture of butadiene and a monomer of esters of nitriles of acrylic acids is treated in an aqueous medium containing an emulsifying agent, an oxidant and 0.5 to 3.0 parts per million of copper in solution to obtain polymerization.

U.S.P. 2,371,849, Process for the Polymerization of Diolefins. W. A. Schulze and W. N. Axe to Phillips Petroleum Company.

An aliphatic conjugated diolefin of the type of butadiene is contacted with a liquid addition compound of BF_3 and an aliphatic monohydric alcohol in the presence of a large volume of a paraffin hydrocarbon as an inert diluent. Preferably a paraffin hydrocarbon of from 4-8 C atoms is used. The concentration of unreacted olefin in the reaction zone may be maintained at less than 10 volume percent of the diluent phase throughout the reaction. Proportions of 0.5 to 1 mol. BF_3 per mol of alcohol give a suitable addition compound. The treating temperature may be kept within the range of 30-120°F.

U.S.P. 2,373,725. Synthetic Hydrocarbon Resins and Process for Making the the Same. Alger L. Ward to United Gas Improvement Company.

A hydrocarbon fraction obtained from light oil produced during the pyrolytic decomposition of petroleum oil for the manufacture of combustible gas which is free from substantial amounts of oxygen-containing compounds, and has 5 percent and 90 percent boiling points between 167.4°C. and 173.2°C. and contains a plurality of unsaturated hydrocarbons, is polymerized by contacting it with a readily hydrolyzable metallic halide catalyst, e.g. a BF_3-organic solvent complex or an $AlCl_3$-organic solvent complex.

U.S.P. 2,374,272. Olefin Polymerization Process. M. T. Carpenter and C. F. Feuchter to Standard Oil Company (Indiana).

Olefin hydrocarbons, such as isobutylene, are polymerized in the liquid state with a vaporous metal halide catalyst, such as BF_3, by first pre-cooling a stream of the liquid hydrocarbon to the desired reaction temperature, then introducing the catalyst into this stream and immediately thereafter rapidly cooling and agitating the obtained mixture. The reaction products containing the catalyst are subjected to vacuum stripping. The vaporous catalyst is recovered overhead and recycled to the polymerization zone. The polymer and unreacted hydrocarbons are withdrawn from the vacuum stripping zone and separated by heating above the boiling point of the unreacted hydrocarbons.

U.S.P. 2,376,985. Production of Styrene from Butadiene. Vanderveer Voorhees to Standard Oil Company.

Butadiene is subjected to polymerization conditions and a butadiene dimer fraction is separated from the polymerization products. This dimer fraction is aromatized by treating it with an aromatizing catalyst at 450-800°C. and a space velocity of 1-10 volumes of dimer fraction per hour per volume of catalyst. The dimer is thereby converted into styrene and ethyl benzene. The styrene is recovered and the ethyl benzene is recycled to the aromatizing operation. The polymerization of butadiene to the dimer is effected by heating it for a short time at about 250-500°C. under atmospheric or slightly higher pressure in the presence of a catalyst, such as Al_2O_3, MgO, or the like.

U.S.P. 2,377,266. Production of Synthetic Lubricating Oil. James A. Reid to Phillips Petroleum Company.

Low-molecular-weight aliphatic monoolefins, such as ethylene and propylene, are polymerized in the absence of catalysts at 315-400°C. under a pressure of 3500-6000 psi for a period sufficient to polymerize between 30 and 60 percent of the normally gaseous olefins charged. A polymer fraction with a boiling range

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Type FLDC Explosion-Proof Secondary Breaker Condulet
Type FLS Explosion-Proof Switch Condulet
Type DXE Condulet with Two Switches
Type GSB Three-Gang Vaportight Condulet with Switches
Type EGP Explosion-Proof Push Button Station and Pilot Light Condulet for Panel Mounting
Type FST Threadless Condulet with Switch
Type FA Four-Gang Watertight Safety Switch Condulet
Type ZT Safety Switch Condulet
Type WMK Raintight Safety Switch Condulet
Type WMKS Raintight Safety Switch and Interlocking Receptacle Condulet
Type FSQC Explosion-Proof Interlocked Receptacle and Switch Condulet
Type GUB Explosion-Proof Motor Starting Switch Condulet
Type FS Condulet with Pilot Light, Switch and Plug Receptacle
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U.S.P. 2,377,411. Polymerization of Hydrocarbons. Frederick E. Frey to Phillips Petroleum Company.

Two or more olefins which differ in inherent reactivity are contacted with a solid polymerization catalyst. The different olefins are maintained in definite and different concentrations, the more reactive kinds being present in lower concentration. The more reactive kind may be supplied in a series of increments to the catalyst whereby the desired concentration is maintained constant, olefin being replaced as it is consumed. Copolymers of the different kinds of olefins are obtained in this manner.

U.S.P. 2,377,779. Process for Polymerizing Ethylene. W. E. Hanford, J. R. Roland and H. S. Young to E. I. du Pont de Nemours & Company.

Substantially oxygen-free ethylene is heated in the presence of a normally liquid non-polymerizable organic medium in contact with an organo lithium compound and in the absence of hydrogenating catalysts. Normally solid polymers of ethylene are produced. The catalyst may consist of alkyl or aryl lithium compounds.

U.S.P. 2,379,431. Polymerization of Butadienes. Charles F. Fryling to The B. F. Goodrich Company.

The polymerization of butadiene —1,3 in the form of an aqueous emulsion in the presence of an organic base containing a long carbon chain proceeds more rapidly on addition of an activator comprising a compound ionizable to yield copper ions and a compound ionizable to yield bisulfite ions. Not over 0.0001 percent of copper in the form of ionizable compound and not over 1 percent of bisulfite in the form of its ionizable compound, both based on the polymerizable material, are required.

U.S.P. 2,379,656. Catalytic Polymerization of Unsaturated Organic Compounds. Robert F. Ruthruff.

The catalytic polymerization of isobutene is carried out by means of an unstable boron halide complex as the catalyst. A temperature below 0°C. is used, and the boron halide complex employed is exhibiting an equilibruim dissociation pressure of at least 5mm. at —70°C. A boron fluorideacetyl chloride complex, a boron fluoride-chloral complex or a boron fluoride-succinic anhydride may be used as suitable catalysts.

U.S.P. 2,379,728. Methods of Preparing Polymerization Products. E. Lieber and H. T. Rice to Standard Oil Development Company.

Aliphatic olefins with less than 10 carbon atoms per mol are polymerized in liquid phase in the presence of a small amount of a Friedel-Crafts catalyst. A viscous oil is produced which has pour-depressing properties when added to waxy mineral lubricating oils in small amounts. An inert hydrocarbon solvent

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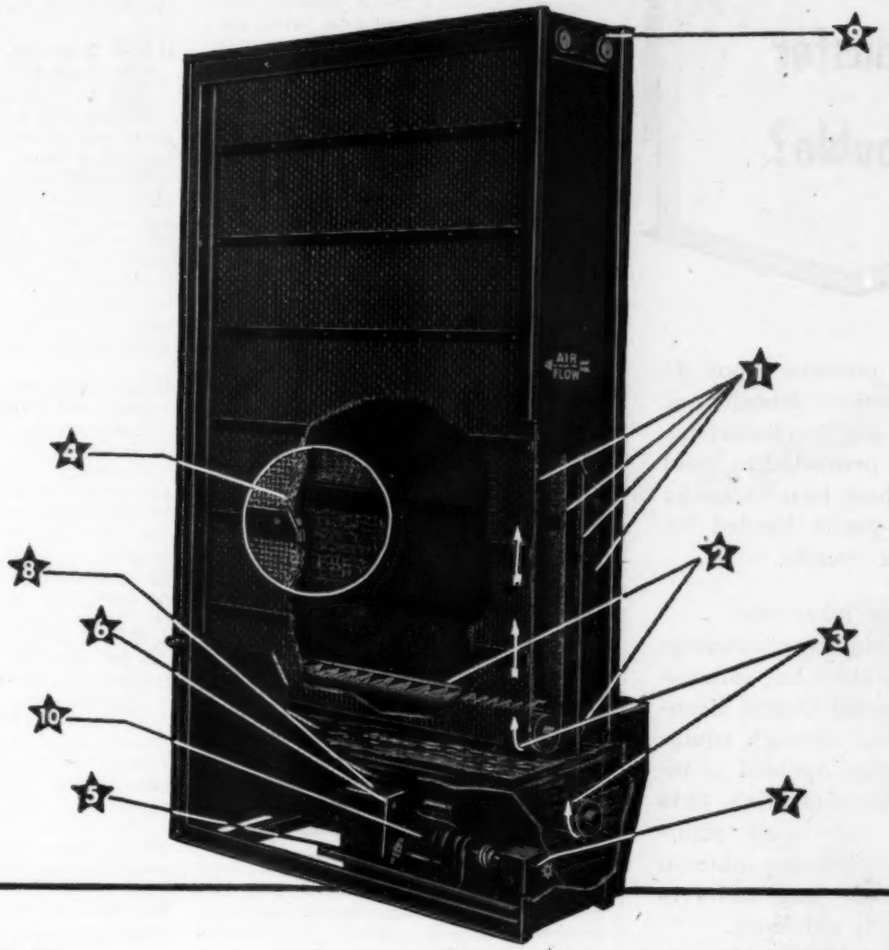

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may be used for the olefins. The reaction temperature may range from room temtemperature to about 200°F.

U.S.P. 2,380,358. Polymerization of Olefins. J. Anderson, W. H. Peterson and S. M. Mc.Alister to Shell Development Company.

Normally gaseous olefins, particularly ethylene, are polymerized to straight-chain olefins having at least 4 carbon atoms, particularly butylenes, by means of a catalyst comprising activated carbon and a reduced metal selected from the 8th group of the periodic table, particularly cobalt and nickel. The reaction is carried out at a temperature from 35°-150°C. and a pressure from 300-900 psi. Copolymerization of ethylene with its higher homologues, particularly with propylene and the butylenes may also be carried out in this manner.

U.S.P. 2,380,400. Polymerization of Butadiene —1,3 Hydrocarbons. George L. Browning, Jr. to The B. E. Goodrich Company.

Polymers more nearly resembling natural crude rubber than the usual polymers may be produced by emulsion polymerization of butadiene —1,3 hydrocarbons by means of so-called "modifiers" consisting of compounds containing the group

$$\left(-X-\overset{\overset{S}{\|}}{C}-S- \right)_3 = P = X$$

wherein X represents oxygen or sulfur. For instance tris (alkoxythiono) trithiophosphate, tris (alkoxythiono) tetrathiophosphate, etc., may be used for this purpose. Mixtures of a butadiene —1,3 hydrocarbon and a smaller amount of a monomer copolymerizable therewith or of acrylonitrile, or of styrene can also be treated in this manner. "Modifiers" of the indicated kind can be prepared by the reaction of an alkali metal xanthate with a phosphorous oxyhalide or a phosphorous thiohalide.

U.S.P. 2,380,471. Polymerization of Butadiene —1,3 Hydrocarbons. Waldo L. Semon to The B. F. Goodrich Company.

Polymers more nearly resembling crude rubber than the usual polymers are produced by emulsion polymerization of butadiene —1,3 in the presence of "modifiers" consisting of compounds containing the group

$$-X-\overset{\overset{S}{\|}}{C}-S-\overset{\overset{X}{\|}}{C}-S-\overset{\overset{S}{\|}}{C}-X-$$

wherein X represents oxygen or sulfur. Compounds containing this group may be prepared by the reaction of an alkali metal xanthate with thiophosgene.

U.S.P. 2,380,614. Method of Making Catalysts. Waldo L. Semon to The B. F. Goodrich Company.

Heavy metal pyrophosphates to be used as catalysts for polymerization reactions are obtained in a high degree of purity by reacting in aqueous solution an alkali metal heavy metal oxalate and an alkali metal pyrophosphate, such as alkali metal ferri oxalate and sodium pyrophosphate.

U.S.P. 2,383,627. Polymerization Catalyst. R. M. Thomas, D. C. Field and H. C. Reynolds Jr. to Jasco Incorporated.

A catalyst for the low-temperature polymerization of olefinic material at temperatures between —10° and 150°C. is obtained by dissolving a Friedel-Crafts catalyst, such as aluminum chloride, in an alkyl halide with less than 3 carbon atoms/mol at a temperature above —23°C. and then cooling the solution to a temperature between —20°C. and the freezing point of the alkyl halide e.g. —78°C. The cooled solution is finally passed through an alkaline solid, such as sodium hydroxide. The invention is based on the discovery that at temperatures below —23°C., hydrogen chloride remains reactive with alkaline bodies, while aluminum chloride becomes relatively non-reactive with such bodies.

U.S.P. 2,381,198. Catalytic Polymerization of Olefins. G. C. Bailey and J. A. Reid to Phillips Petroleum Company.

Olefins are polymerized in the presence of a catalyst comprising an active form of a metal oxide of the iron group. This metal oxide is activated by heating to a temperature above 400°C. Simple aliphatic olefin hydrocarbon polymers of higher molecular weight are formed by such polymerization. Nickel oxide is the preferred metal oxide used, and it may be supported on material having extensive surface area, such as kieselguhr, alumina, charcoal, etc.

U.S.P. 2,381,481. Hydrocarbon Conversions and Catalysts Therefor. John A. Anderson to Standard Oil Company (Indiana).

Normally gaseous hydrocarbons are converted to normally liquid products by subjecting them to polymerization in the presence of a catalyst prepared by treating an alumina gel with a complex fluoric acid, such as fluoboric, fluosilicic or fluotitanic acid.

U.S.P. 2,382,117. Manufacture of Motor Fuel. Halsted Rogers Warrick to The Texas Company.

Normally gaseous saturated hydrocarbons such as ethane and propane, or hydrocarbon mixtures containing them are thermally converted at elevated temperature to form a synthetic mixture containing ethylene and higher olefin hydrocarbons as well as converted hydrocarbons boiling within the range suitable for motor fuel. This mixture is treated to remove the normally liquid polymer gasoline hydrocarbons and to segregate a normally gaseous hydrocarbon fraction containing ethylene and higher olefins. This segregated fraction is subjected to catalytic polymerization so as to convert substantially all of the propylene and butylene present to polymer gasoline. The unconverted material comprising ethylene substantially free from propylene is then subjected to alkylation with isobutane in the presence of a suitable alkylation catalyst.

U.S.P. 2,383,055. Polymerization of Conjugated Dienes. Charles F. Fryling to The B. F. Goodrich Company.

Conjugated butadiene hydrocarbons alone or in admixture with other compounds polymerizable therewith are polymerized in aqueous emulsion in presence of inorganic compounds containing both sulfur and oxygen which compounds normally function as reducing agents. Included in the class of these inorganic compounds are the lower oxides of sulfur, the oxyacids derived therefrom, and the salts, acid chlorides and other derivatives of these acids. The preferred compounds are SO_2, H_2SO_3, Na_2SO_3 or other water-soluble sulfites, and bisulfites, the water-soluble sulphoxylates (hydrosulfites) and the wa-

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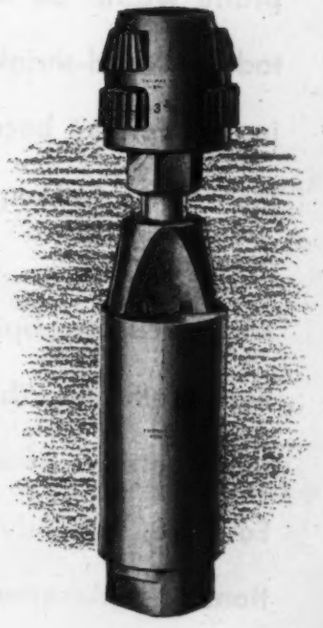

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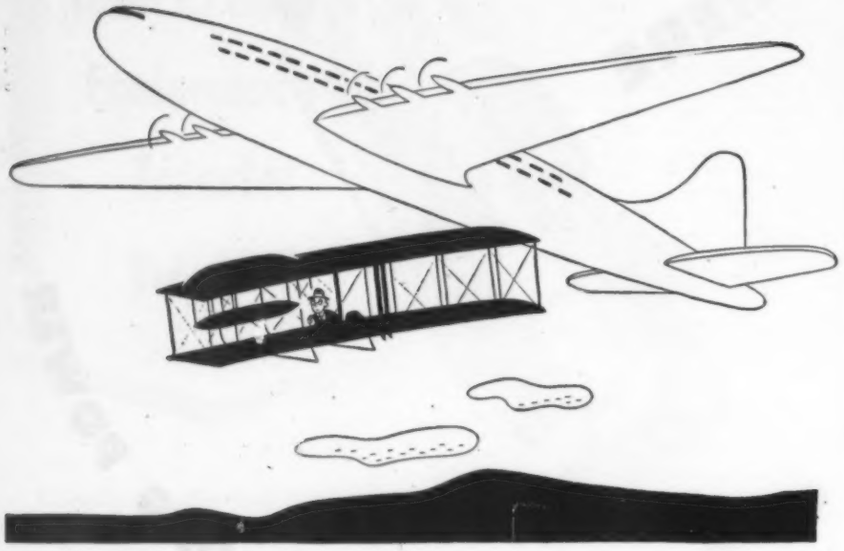

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ter-soluble dithionites (hyposulfites). The hydrocarbon mixture to be polymerized may be a monomer mixture including a conjugated butadiene and a comonomer containing the structure $CH_2=C<$ wherein at least one of the dangling valences is connected to a negative group, such as methyl methacrylate or acrylonitrile.

U.S.P. 2,383,425. Polymerization of Unsaturated Organic Compounds. William D. Stewart to The B. F. Goodrich Company.

Butadiene —1,3 alone or in admixture with other copolymerizable materials, particularly with unsaturated compounds which contain a single olefinic double bond, such as styrene or acrylonitrile, are polymerized in aqueous emulsion in the presence of a water-soluble complex compound containing a central heavy metal atom connected by a coordinating valence to a nitrogen-containing coordiating group. Examples of such catalyzing compounds are alkali metal cobaltinitrite, alkali metal nitroprusside, potassium cobaltic cyanide, etc. They are used in quantities of from 0.01 to 1 percent by weight based on the material polymerized.

U.S.P. 2,384,568. Polymerization Products. Waldo L. Semon to The B. F. Goodrich Company.

A diene hydrocarbon or a mixture of diene hydrocarbons of the general formula $CH_2=\underset{X}{C}-\underset{X}{C}=\underset{C}{CH}$ wherein each X may be hydrogen or methyl are polymerized with polymerizable vinyl compounds in the presence of an oxygen-containing compound having in its structure at least two polymerizable not conjugated double bonds. Polymers with improved plastic properties may be obtained in this way. The materials to be copolymerized with the diene hydrocarbons are preferably esters which contain at least two polymerizable $CH_2=C<$ groups separated by the ester linkage, such as polyallyl esters of polybasis acids, e.g. diallyl adipate. The polymerization may be carried out in the form of an emulsion at temperatures between 30° —70°C. in the presence of a catalyst, like benzoyl peroxide.

U.S.P. 2,384,916. Method of Producing High-Molecular-Weight Iso-Olefin Polymers. Robert L. Holmes to Jasco, Inc.

Iso-olefins, such as isobutylene, are polymerized to high-molecular-weight hydrocarbons by treatment with an active inorganic halide catalyst of the Friedel-Crafts type, such as BF_3, in the presence of a small quantity of a promoter consisting of an aliphatic ether, ester, or ketone, having a total of less than 11 carbon atoms. The promoter increases the yield of higher-molecular-weight polymers. The polymerization temperature employed is —40° to —103°C.

U.S.P. 2,395,190. Polymerization of Conjugated Diene Hydrocarbons. George L. Browning to The B. F. Goodrich Company.

Conjugated diene hydrocarbons, such as butadiene, are converted to polymers more nearly resembling natural crude rubber than the usual polymers, by polymerization in an aqueous emulsion in the presence of a tetra-alkyl thiuram sulfide in which the alkyl groups contain a total of at least 12 carbon atoms. A monomer copolymerizable with the

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diene may be added, such as styrene or acrylonitrile.

U.S.P. 2,385,237. Hydrocarbon Polymerization Process. E. E. Stahly and F. B. Johson to Standard Oil Development Company.

Isobutylene and its normally liquid polymers, chiefly diisobutylene and triisobutylene, are reacted with normal butylenes in the presence of a polymerization catalyst, such as H_2SO_4, to form products which are similar in structure to copolymers of isobutylene and normal butylenes. These copolymers may be hydrogenated to form high-octane-number blending ingredients for aviation fuels. The H_2SO_4 used as the catalyst is of about 60 percent to 75 percent concentration, and the polymerization temperature is between 150°-250°F. The polymerization is carried out in several steps; in the first step isobutylene and n-butylene are contacted in a molar ratio of at least 1. After contact with the catalyst for not more than 20 minutes, an amount of n-butylene is added which will produce in the mixture a total amount of n-butylene equal to at least 2 mols per mol of diisobutylene present. This mixture is then contacted in a second reaction zone with fresh catalyst for a period of 2-3 hours.

U.S.P. 2,385,609. Process of Polymerizing Olefins. Alfred Clark and Richard S. Shutt to Battelle Memorial Institute.

Normally gaseous mixtures containing ethylene, propylene and butylene are passed through a reactor in contact with a catalyst of a zinc, copper or cadmium chromite at temperatures between 200 and 600°C. and under pressures of 200-1500 psi. The olefins are polymerized simultaneously under these conditions.

U.S.P. 2,387,543. Polymerization Catalysts. R. M. Thomas and J. F. Nelson to Jasco, Inc.

The polymerization of olefinic materials at temperatures between —10° and —150°C. in the presence of a catalyst comprising the complex formed by reacting a Friedel-Crafts metal halide with a complex-forming organic solvent, such as nitromethane or di-isobutylene, is carried out in the presence of an alkyl chloride with less than 3 carbon atoms as a solvent for the catalyst complex.

U.S.P. 2,387,784. Polymerization Process for Normal Olefins. R. M. Thomas and H. C. Reynolds to Standard Oil Development Company.

Normal olefins having 3 to 6 C atoms are polymerized in the presence of a Friedel-Crafts type catalyst dissolved in an alkyl halide having less than 4 C atoms per mol. The olefin is cooled to a temperature below —10°C. and mixed with about 1 part of the cooled catalyst solution (1-100 percent conc.) per 0.05 to 4 parts of olefin. High-molecular-weight polymers are obtained in this way.

U.S.P. 2,388,225. Process for Polymerizing Olefinic Material. R. E. Brooks, M. D. Peterson, and A. G. Weber to E. I. du Pont de Nemours & Company.

Ethylene alone or in admixture with at least one other polymerizable compound, such as vinyl acetate is polymerized at elevated pressure and temperature in the presence of water and a specific catalyst combination. This combination consists of an alkali persulfate and a reagent which will insure the reaction to be carried out at pH in the range of from 7 to 11. Suitable reagents to be used alone or in mixture, are borax, sodium bicarbonate, potassium bicarbonate, sodium phosphate and the like. The quantity of persulfate employed can vary from 0.001 to 1.0 percent or higher, and the quantity of the buffer can vary from 0.01 to 10.0 percent. No dispersing medium is used in this process. Pressure of 300 to 1500 atmospheric and temperatures between 60° and 250°C. are employed. The final products from this process are obtained in a semi-dispersed form and do not agglomerate so that they may be readily removed from the reaction vessel.

U.S.P. 2,388,514. Modifiers for Polymerization of Butadiene —1,3 hydrocarbons. B. M. G. Zwicker and W. D. Stewart to The B. F. Goodrich Company.

Butadiene —1,3 either alone or in admixture with other organic compounds copolymerizable therewith, is polymerized in aqueous emulsion in the presence of a compound of the formula $R-(S)_n-X$ wherein R is a thiazol-2 radical, n is an integer from 1 to 4 and X is a monovalent organic radical other than R, having its monovalency on a carbon atom. A water-soluble compound of heavy metal of group VIII and the first long period of the periodic table may be added. The polymers obtained are more plastic than those obtained by means of the usual catalysts or modifiers.

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